Phosphoramidate-assisted alkyne activation: Probing the mechanism of proton shuttling in a *N,O*-chelated Cp*Ir(III) complex

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Supporting Information

1. Contents

2. Computational methods

2.1. General considerations

Initial optimisations were performed at the (RI-)BP86/SV(P) level, followed by frequency calculations at the same level. Transition states were located by initially performing a constrained minimisation (by freezing internal coordinates that change most during the reaction) of a structure close to the anticipated transition state. This was followed by a frequency calculation to identify the transition vector to follow during a subsequent transition state optimisation. A final frequency calculation was then performed on the optimised transition-state structure. All minima were confirmed as such by the absence of imaginary frequencies and all transition states were identified by the presence of only one imaginary frequency. All transition states were verified as connecting to the expected adjacent minima using the DRC module of TURBOMOLE (using an initial distortion length of 100, 50 cycles and a damping factor of 1). Dynamic reaction coordinate (DRC) calculations aim to follow a classical trajectory from a transition state to the minima on either side of it by moving along its imaginary vibrational mode.[1,2] DRC calculations are similar to, but computationally less expensive than, intrinsic reaction coordinate (IRC) calculations, which attempt to find the minimum energy path (MEP) from the transition state to connecting minima.

Single-point calculations on the (RI-)BP86/SV(P) optimised geometries were performed using the hybrid PBE0 functional and the flexible def2-TZVPP basis set. The (RI-)PBE0/def2-TZVPP SCF energies were corrected for their zero-point energies, thermal energies and entropies (obtained from the (RI-)BP86/SV(P)-level frequency calculations). In all calculations, a 60 electron quasi-relativistic ECP replaced the core electrons of Ir. No symmetry constraints were applied during optimisations. All calculations were performed using the TURBOMOLE V6.40 package using the resolution of identity (RI) approximation.[3-13] Solvation effects were modelled using the COSMO module of TURBOMOLE.[14] The dielectric constant used was for dichloromethane (8.93 at 298 K).[15]

Both enthalpies and Gibbs energies at 298.15 K are shown on the PES'. Gibbs energy changes are discussed in the main section of the manuscript. The difficulty in assessing entropy changes in solution from gas-phase calculations is acknowledged,[16-18] but not of great importance here, as all key steps are unimolecular rearrangements where entropy changes will be small.

Single-point DFT-D3 corrections (on the (RI-)BP86/SV(P) geometries) have been applied at the PBE0-D3 level using Grimme's DFT-D3 V3.0 Rev 2 program (with BJ-damping)[19,20] and data presented in the main section of the paper includes this correction. Both DFT-D3 and DFT data are presented in the tables and PES given below.

Structures were visualised and modified using Facio,[21] Jmol,[22] and gOpenMol.

2.2. Explanation of nomenclature

The naming system used in the supporting information is identical to that found in the manuscript, for complexes discussed both in the text and on the potential energy surface in Figure 2. Where more than one isomer has been considered, this is designated with the following:

- ***E*** or ***Z*** – denotes the stereochemistry of the alkenyl group in isomers of complexes **5a** and **5b**
- **a**, **b**, **c** refer to different regioisomers of a particular complex
- **i**, **ii**, **iii**, **iv**, **v** refer to different conformational isomers of the same complex

Multiple alkyne R groups were investigated for the final two complexes **5a** and **5b**. The R group for these complexes is written in parentheses when it is not Me.

In the tabulated energies, the isomers marked ***** are those used in the discussion and PES in the manuscript.

2.3. Full potential energy surface

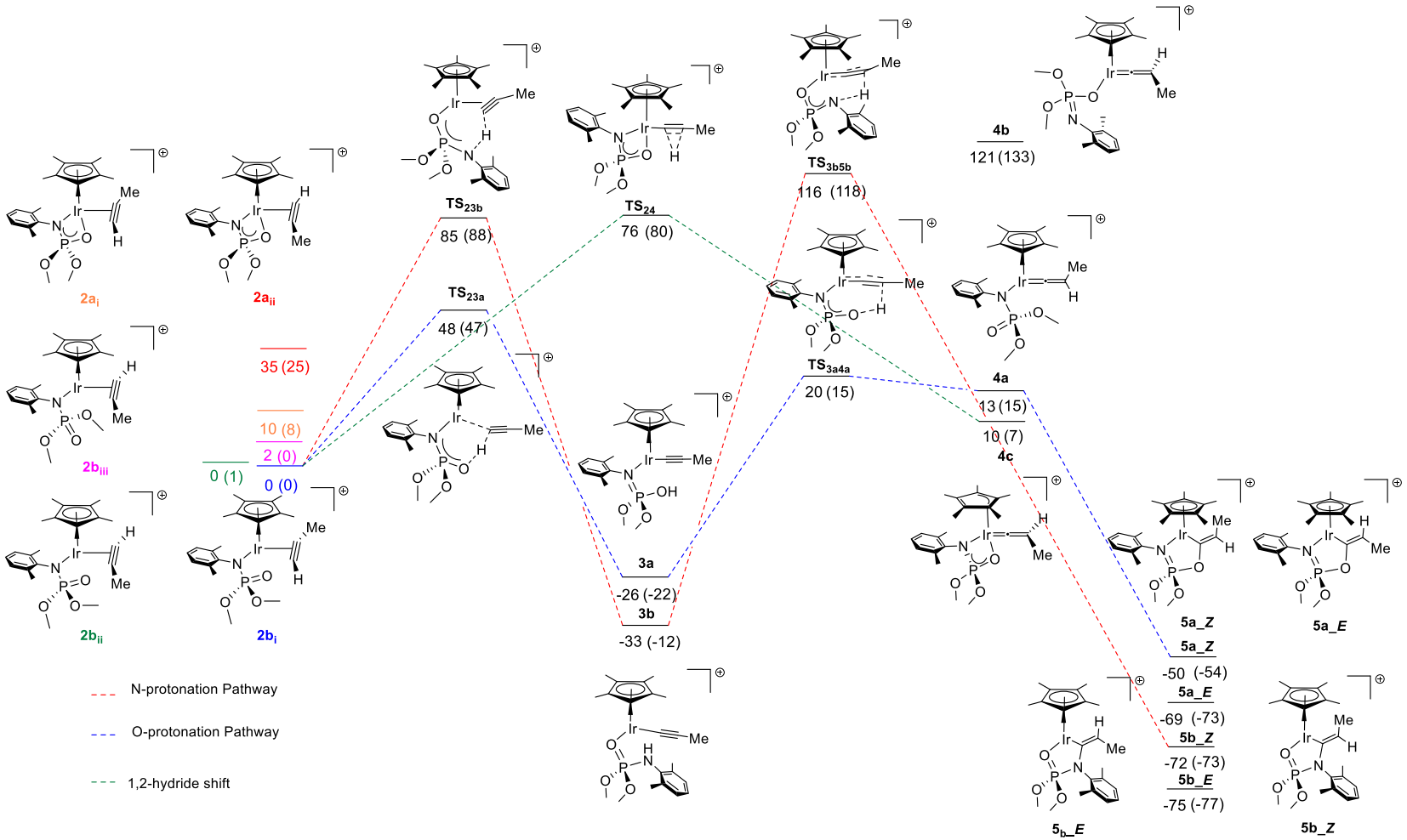


Figure S1: Full potential energy surface for the study presented in the main section. Gibbs energies, relative to **2bi**, are shown in kJ mol^{-1} at the (RI)-PBE0-D3/def2-TZVPP//(RI)-BP86/SV(P) level in CH_2Cl_2 (COSMO solvation). Relative enthalpies, at the same level, are also shown in brackets

2.4. Potential energy surface for Cp*-protonation and oxidative-addition pathways

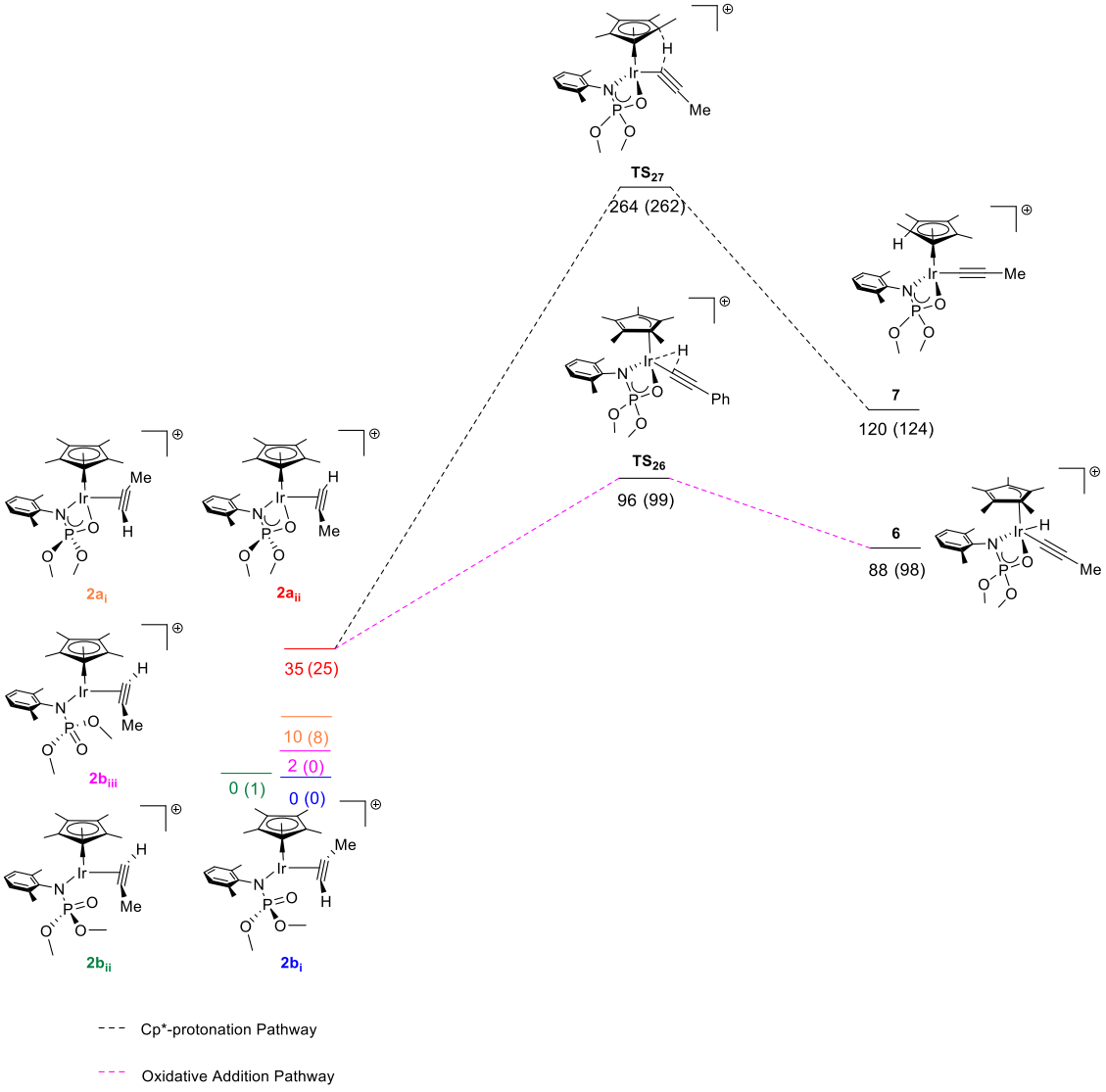


Figure S2: Potential energy surface for the Cp*-protonation and oxidative addition pathways considered for the formation of **5**. Gibbs energies, relative to **2bi**, are shown in kJ mol^{-1} at the (RI)-PBE0-D3/def2-TZVPP//(RI)-BP86/SV(P) level in CH_2Cl_2 (COSMO solvation). Relative enthalpies, at the same level, are also shown in brackets.

3. Tabulated energies

Table S1: SCF and COSMO (DCM ε=8.93) corrected energies with vibrational corrections at the (RI)-BP86/SV(P) level

BP86/SV(P)									
		Vibrational Frequencies							
	SCF (a.u.)	COSMO (CH_2Cl_2) (a.u.)	ZPE (a.u.)	Chem. Pot. (kJ mol^{-1})	Energy (kJ mol^{-1})	Entropy (kJ K^{-1} mol^{-1})	ln q(vib)	Entropy at 1 mol dm^{-3} (kJ K^{-1} mol^{-1})	DFT-D3 corr. (a.u.)
$2b_{iii}$	-1622.1082	-1622.1593	0.5072	1151.89	1429.61	0.9398	35.84	0.9131	-0.169
$2b_{i}$	-1622.1082	-1622.1593	0.5071	1149.75	1429.42	0.9463	36.56	0.9196	-0.169
$2b_{ii}$	-1622.1057	-1622.1578	0.5069	1148.97	1429.25	0.9484	36.63	0.9217	-0.169
$2a_{ii}$	-1622.0985	-1622.1489	0.5091	1162.23	1432.08	0.9134	33.66	0.8867	-0.166
$2a_{i}$	-1622.1043	-1622.1537	0.5079	1153.36	1430.62	0.9383	35.95	0.9116	-0.165
3_a	-1622.1137	-1622.1608	0.5071	1145.90	1429.40	0.9592	38.02	0.9325	-0.161
3_b	-1622.1231	-1622.1711	0.5080	1133.23	1433.99	1.0171	43.82	0.9904	-0.143
3_c	-1622.0794	-1622.1292	0.5081	1142.84	1432.81	0.9809	40.31	0.9542	-0.160
6	-1622.0650	-1622.1148	0.5056	1142.20	1425.90	0.9598	37.93	0.9331	-0.161
TS_{23a}	-1622.0933	-1622.1438	0.5009	1142.07	1420.97	0.9437	36.85	0.9170	-0.165
TS_{23b}	-1622.0774	-1622.1272	0.5051	1135.85	1418.60	0.9567	38.16	0.9300	-0.158
TS_{23c}	-1622.0268	-1622.0766	0.4998	1139.96	1417.36	0.9387	36.06	0.9120	-0.159
TS_{26}	-1622.0645	-1622.1141	0.5045	1138.73	1421.49	0.9567	37.88	0.9300	-0.162
TS_{24}	-1622.0723	-1622.1240	0.5035	1136.19	1419.81	0.9596	38.11	0.9329	-0.157
TS_{3a4}	-1622.1054	-1622.1539	0.5041	1131.82	1408.31	0.9357	35.95	0.9090	-0.162
TS_{3b5b}	-1622.0746	-1622.1301	0.5040	1129.89	1421.58	0.9867	41.00	0.9600	-0.144
4_a	-1622.1060	-1622.1596	0.5077	1149.88	1430.75	0.9503	37.07	0.9236	-0.163
4_b	-1622.0795	-1622.1289	0.5065	1137.40	1429.16	0.9869	40.75	0.9602	-0.151
4_{ci}	-1622.1131	-1622.1619	0.5085	1154.07	1431.86	0.9400	36.25	0.9133	-0.160
4_{cii}	-1622.1143	-1622.1631	0.5088	1155.76	1432.37	0.9361	35.92	0.9094	-0.160
5_a_*E*	-1622.1464	-1622.1933	0.5106	1160.65	1435.91	0.9315	35.85	0.9048	-0.159
5_b_*E*	-1622.1504	-1622.1973	0.5109	1159.48	1437.04	0.9393	36.53	0.9126	-0.155
5_a_*Z*	-1622.1381	-1622.1852	0.5104	1160.13	1435.41	0.9316	35.85	0.9049	-0.161
5_b_*Z*	-1622.1488	-1622.1957	0.5106	1158.13	1436.59	0.9423	36.76	0.9156	-0.154
5_a_*E* (Ph)	-1813.7579	-1813.8063	0.5631	1284.40	1581.63	1.005	40.77	0.9785	-0.180
5_b_*E* (Ph)	-1813.7562	-1813.8042	0.5629	1283.44	1581.42	1.008	40.98	0.9811	-0.180
5_a_*E* (*p*-^{t}Bu)	-1970.8821	-1970.9293	0.6717	1552.73	1881.67	1.112	46.87	1.085	-0.204
5_b_*E* (*p*-^{t}Bu)	-1970.8802	-1970.9266	0.6716	1551.74	1881.64	1.115	47.21	1.088	-0.204
5_a_*E* (Cy)	-1817.3502	-1817.3961	0.6302	1454.64	1762.19	1.040	43.09	1.013	-0.186
5_b_*E* (Cy)	-1817.3541	-1817.3998	0.6302	1453.35	1762.89	1.047	43.62	1.020	-0.186
5_a_*E* (^{t}Bu)	-1739.9831	-1740.0293	0.5923	1362.44	1661.08	1.010	40.53	0.9833	-0.180
5_b_*E* (^{t}Bu)	-1739.9769	-1740.0231	0.5927	1362.25	1662.06	1.014	40.96	0.9872	-0.180

Table S2: Relative electronic energies, enthalpies and gibbs energies in the gas phase, solvent (COSMO, DCM ε=8.93) and dispersion (DFT-D3) corrected energies at the (RI)-BP86/SV(P) level

BP86/SV(P)										
		Gas Phase 298.15 K			COSMO CH_2Cl_2 298.15 K			DFT-D3 COSMO CH_2Cl_2 298.15 K		
	Electronic Energy (kJ mol^{-1})	Rel H (kJ mol^{-1})	Rel S (J K^{-1} mol^{-1})	Rel G (kJ mol^{-1})	Rel H (kJ mol^{-1})	Rel S (J K^{-1} mol^{-1})	Rel G (kJ mol^{-1})	Rel H (kJ mol^{-1})	Rel S (J K^{-1} mol^{-1})	Rel G (kJ mol^{-1})
$2b_{iii}$	0	0	-7	2	0	-7	2	0	-7	2
$2b_{i}$	0	0	0	0	0	0	0	0	0	0
$2b_{ii}$	7	6	2	6	4	2	3	3	2	2
$2a_{ii}$	26	28	-33	38	30	-33	40	37	-33	46
$2a_{i}$	10	11	-8	14	16	-8	18	27	-8	29
3_a	-14	-14	13	-18	-4	13	-8	16	13	12
3_b	-39	-34	71	-56	-27	71	-48	40	71	19
3_c	76	79	35	69	82	35	72	107	35	96
6	114	110	14	106	113	14	109	133	14	129
TS_{23a}	39	31	-3	32	32	-3	33	43	-3	43
TS_{23b}	81	70	10	67	73	10	70	103	10	100
TS_{23c}	214	202	-8	204	205	-8	207	230	-8	232
TS_{26}	115	107	10	104	111	10	107	129	10	126
TS_{24}	94	85	13	81	83	13	79	115	13	111
TS_{3a4}	7	-14	-11	-11	-7	-11	-4	10	-11	13
TS_{3b5b}	88	80	40	68	69	40	57	134	40	122
4_a	6	7	4	6	1	4	-1	16	4	15
4_b	75	75	41	63	79	41	67	125	41	113
4_{ci}										
4_{cii}	-16	-13	-10	-10	-7	-10	-4	16	-10	19
5_a_*E*	-100	-94	-15	-89	-83	-15	-79	-58	-15	-54
5_b_*E*	-111	-103	-7	-101	-92	-7	-90	-56	-7	-54
5_a_*Z*	-90	-72	-15	-68	-62	-15	-58	-42	-15	-38
5_b_*Z*	-119	-99	-4	-98	-89	-4	-87	-50	-4	-48
5_a_*E* (Ph)	0	0	0	0	0	0	0	0	0	0
5_b_*E* (Ph)	5	9	3	9	5	3	5	6	3	5
5_a_*E* (*p*-^{t}Bu)	0	0	0	0	0	0	0	0	0	0
5_b_*E* (*p*-^{t}Bu)	5	5	3	4	7	3	6	6	3	5
5_a_*E* (Cy)	10	9	-7	11	9	-7	11	9	-7	11
5_b_*E* (Cy)	0	0	0	0	0	0	0	0	0	0
5_a_*E* (^{t}Bu)	0	0	0	0	0	0	0	0	0	0
5_b_*E* (^{t}Bu)	16	17	4	16	17	4	16	17	4	16

Table S3: SCF and COSMO (DCM ε=8.93) corrected energies with vibrational corrections at the (RI)-PBE0/def2-TZVPP//(RI)-BP86/SV(P) level

PBE0/def2-TZVPP//BP86/SV(P)									
		Vibrational Frequencies							
	SCF (a.u.)	COSMO (CH_2Cl_2) (a.u.)	ZPE (a.u.)	Chem. Pot. (kJ mol^{-1})	Energy (kJ mol^{-1})	Entropy (kJ K^{-1} mol^{-1})	ln q(vib)	Entropy at 1 mol dm^{-3} (kJ K^{-1} mol^{-1})	DFT-D3 corr. (a.u.)
$2b_{iii}$	-1621.877892	-1621.931506	0.507217	1152	1430	0.9398	35.84	0.9131	-0.0935
***** **$2b_{i}$**	-1621.877852	-1621.931413	0.507084	1150	1429	0.9463	36.56	0.9196	-0.0935
$2b_{ii}$	-1621.876071	-1621.930906	0.506855	1149	1429	0.9484	36.63	0.9217	-0.0937
$2a_{ii}$	-1621.871853	-1621.924157	0.509112	1162	1432	0.9134	33.66	0.8867	-0.0923
$2a_{i}$	-1621.879828	-1621.931052	0.507900	1153	1431	0.9383	35.95	0.9116	-0.0914
***** **3_a**	-1621.895649	-1621.943877	0.507074	1146	1429	0.9592	38.02	0.9325	-0.0894
***** **3_b**	-1621.901981	-1621.951669	0.507980	1133	1434	1.0171	43.82	0.9904	-0.0795
***** **3_c**	-1621.848622	-1621.900302	0.508074	1143	1433	0.9809	40.31	0.9542	-0.0885
6	-1621.834694	-1621.886861	0.505586	1142	1426	0.9598	37.93	0.9331	-0.0895
***** **TS_{23a}**	-1621.861277	-1621.914092	0.500915	1142	1421	0.9437	36.85	0.9170	-0.0898
***** **TS_{23b}**	-1621.848621	-1621.900120	0.505065	1136	1419	0.9567	38.16	0.9300	-0.0871
TS_{23c}	-1621.780506	-1621.832244	0.499820	1140	1417	0.9387	36.06	0.9120	-0.0885
***** **TS_{26}**	-1621.843583	-1621.895168	0.503738	1138	1420	0.9546	37.63	0.9279	-0.0887
***** **TS_{24}**	-1621.849068	-1621.903060	0.503540	1136	1420	0.9596	38.11	0.9329	-0.0878
***** **TS_{3a4}**	-1621.875033	-1621.925387	0.504102	1144	1419	0.9311	35.64	0.9044	-0.0898
***** **TS_{3b5b}**	-1621.836567	-1621.896980	0.503982	1130	1422	0.9867	41.00	0.9271	-0.0799
***** **4_a**	-1621.870008	-1621.926966	0.507651	1150	1431	0.9503	37.07	0.9236	-0.0903
***** **4_b**	-1621.835228	-1621.889809	0.506475	1137	1429	0.9869	40.75	0.9602	-0.0844
4_{ci}	-1621.882579	-1621.933198	0.508494	1154	1432	0.9400	36.25	0.9133	-0.0890
***** **4_{cii}**	-1621.883921	-1621.934563	0.508822	1156	1432	0.9361	35.92	0.9094	-0.0889
***** **5_a_*E***	-1621.918632	-1621.966894	0.510627	1161	1436	0.9315	35.85	0.9048	-0.0883
***** **5_b_*E***	-1621.922746	-1621.971264	0.510935	1159	1437	0.9393	36.53	0.9126	-0.0859
***** **5_a_*Z***	-1621.910189	-1621.958639	0.510420	1160	1435	0.9316	35.85	0.9049	-0.0894
***** **5_b_*Z***	-1621.921753	-1621.970310	0.510643	1158	1437	0.9423	36.76	0.9156	-0.0853
5_a_*E* (Ph)	-1813.495817	-1813.546264	0.563071	1284	1582	1.0052	40.77	0.9785	-0.100
5_b_*E* (Ph)	-1813.494740	-1813.545288	0.562912	1283	1581	1.0078	40.98	0.9811	-0.100
5_a_*E* (*p*-^{t}Bu)	-1970.611079	-1970.660612	0.671671	1553	1882	1.1116	46.87	1.0849	-0.114
5_b_*E* (*p*-^{t}Bu)	-1970.609425	-1970.658670	0.671572	1552	1882	1.1148	47.21	1.0881	-0.114
5_a_*E* (Cy)	-1817.105347	-1817.152694	0.630160	1455	1762	1.0398	43.09	1.0131	-0.104
5_b_*E* (Cy)	-1817.109679	-1817.157121	0.630180	1453	1763	1.0465	43.62	1.0198	-0.104
5_a_*E* (^{t}Bu)	-1739.748719	-1739.796400	0.592294	1362	1661	1.0100	40.53	0.9833	-0.100
5_b_*E* (^{t}Bu)	-1739.742644	-1739.790485	0.592678	1362	1662	1.0139	40.96	0.9872	-0.101

Table S4: Relative electronic energies, enthalpies and gibbs energies in the gas phase, solvent (COSMO, DCM ε=8.93) and dispersion (DFT-D3) corrected energies at the (RI)-PBE0/def2-TZVPP//(RI)-BP86/SV(P) level

PBE0/def2-TZVPP//BP86/SV(P)										
		Gas Phase 298.15 K			COSMO CH_2Cl_2 298.15 K			DFT-D3 COSMO CH_2Cl_2 298.15 K		
	Electronic Energy (kJ mol^{-1})	Rel H (kJ mol^{-1})	Rel S (J K^{-1} mol^{-1})	Rel G (kJ mol^{-1})	Rel H (kJ mol^{-1})	Rel S (J K^{-1} mol^{-1})	Rel G (kJmol^{-1})	Rel H (kJ mol^{-1})	Rel S (J K^{-1} mol^{-1})	Rel G (kJ mol^{-1})
$2b_{iii}$	0	0	-7	2	0	-7	2	0	-7	2
***** **$2b_{i}$**	0	0	0	0	0	0	0	0	0	0
$2b_{ii}$	5	5	2	4	1	2	1	1	2	0
$2a_{ii}$	16	18	-33	28	22	-33	32	25	-33	35
$2a_{i}$	-5	-4	-8	-2	2	-8	5	8	-8	10
3_a	-47	-47	13	-51	-33	13	-37	-22	13	-26
3_b	-63	-59	71	-80	-49	71	-70	-12	71	-33
3_c	77	80	35	70	85	35	75	98	35	88
6	113	110	14	106	113	14	109	124	14	120
TS_{23a}	44	35	-3	36	37	-3	38	47	-3	48
TS_{23b}	77	66	10	63	71	10	68	88	10	85
TS_{23c}	256	244	-8	246	248	-8	251	262	-8	264
TS_{26}	90	81	8	79	86	8	84	99	8	96
TS_{24}	76	66	13	62	65	13	61	80	13	76
TS_{3a4}	7	-3	-15	2	5	-15	10	15	-15	20
TS_{3b5b}	108	101	40	89	83	8	80	118	8	116
4_a	21	22	4	21	13	4	12	21	4	20
4_b	112	112	41	100	-38	41	-50	133	41	121
4_{ci}										
4_{cii}	-16	-13	-10	-10	-5	-10	-2	7	-10	10
5_a_*E*	-107	-101	-15	-96	-87	-15	-82	-73	-15	-69
5_b_*E*	-118	-110	-7	-108	-97	-7	-95	-77	-7	-75
5_a_*Z*	-85	-79	-15	-75	-38	-15	-34	-54	-15	-50
5_b_*Z*	-115	-108	-4	-107	-67	-4	-66	-73	-4	-72
5_a_*E* (Ph)	0	0	0	0	0	0	0	0	0	0
5_b_*E* (Ph)	3	8	3	7	2	3	2	2	3	1
5_a_*E* (*p*-^{t}Bu)	0	0	0	0	0	0	0	0	0	0
5_b_*E* (*p*-^{t}Bu)	4	4	3	3	5	3	4	4	3	3
5_a_*E* (Cy)	11	11	-7	13	11	-7	13	12	-7	14
5_b_*E* (Cy)	0	0	0	0	0	0	0	0	0	0
5_a_*E* (^{t}Bu)	0	0	0	0	0	0	0	0	0	0
5_b_*E* (^{t}Bu)	16	17	4	16	17	4	15	16	4	15

4. Functional dependence of the relative energies of isomers of 5

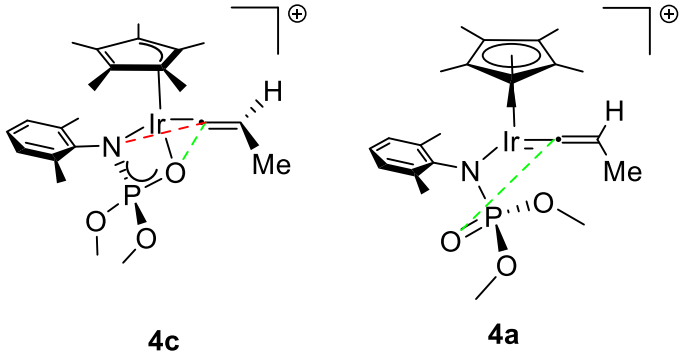
In order to assess the functional dependence of the relative energies of the product, which are important in assessing the thermodynamic preference for the reaction, the electronic structures of isomers of **5** (at the BP86/SV(P) geometries) were optimised at the wB97XD/def2-TZVPP and M06/def2-TZVPP levels using Gaussian 09.[23] The energies of each state, relative to $\mathbf{5}_{a\_E}$ are presented in table S5, alongside data at the PBE0-D3/def2-TZVPP level. For all functionals, the relative energies of the different isomers are very similar and most isomers are essentially isoenergetic within error. This gives some confidence that large functional effects on the thermodynamic preference for the reaction are not seen in this system.

Table S5: Absolute and relative electronic energies for isomers of **5** at different levels of theory.

	PBE0-D3 E_{elec} (a.u.)	Rel. E (kJ mol^{-1})	M06 E_{elec} (a.u.)	Rel. E (kJ mol^{-1})	wB97XD E_{elec} (a.u.)	Rel. E (kJ mol^{-1})
$\mathbf{5}_{a\_E}$	-1622.006945	0	-1622.588944	0	-1623.141522	0
$\mathbf{5}_{b\_E}$	-1622.008624	-4	-1622.589269	-1	-1623.142193	-2
$\mathbf{5}_{a\_Z}$	-1621.999549	19	-1622.582844	16	-1623.135278	16
$\mathbf{5}_{b\_Z}$	-1622.007067	0	-1622.588143	2	-1623.141	1

5. Potential energy surface (PES) scans

All PES scans were carried out using TURBOMOLE within ChemShell 3.7.0. The (RI)-BP86/SV(P) level was used for each point along the scan.[24-26] DL-FIND was used for the optimizations. Figure S2 shows the structures of the two complexes where PES scans were carried out. In **4c** both the N-C distance and the O-C distance was scanned along to determine whether attack of the nitrogen or oxygen at the α-carbon of the vinylidene was possible directly from this isomer. The N-C and O-C distances were fixed at the distances specified in the tables below while the remaining atoms were allowed to relax. In **4a** only the O-C distance was investigated to determine if there was a barrier for the uncoordinated oxygen to attack the α-carbon of the vinylidene.



4c **4a**

Figure S3: Dashed bonds connect the two atoms involved in the scans.

4c N-C distance scan

Table S6: Relative electronic energies of the relaxed PES scan of the N-C distance, 1.22 to 3.12 Å, in **4c** at the (RI)-BP86/SV(P) level

N-C distance (Å)	Relative Electronic Energy (kJ mol^{-1})
3.12	0
3.02	1
2.92	5
2.82	10
2.72	17
2.62	26
2.52	37
2.42	50
2.32	61
2.22	63
2.12	13
2.02	-1
1.92	-17
1.82	-36
1.72	-56
1.62	-76
1.52	-89
1.42	-88
1.32	-57
1.22	27

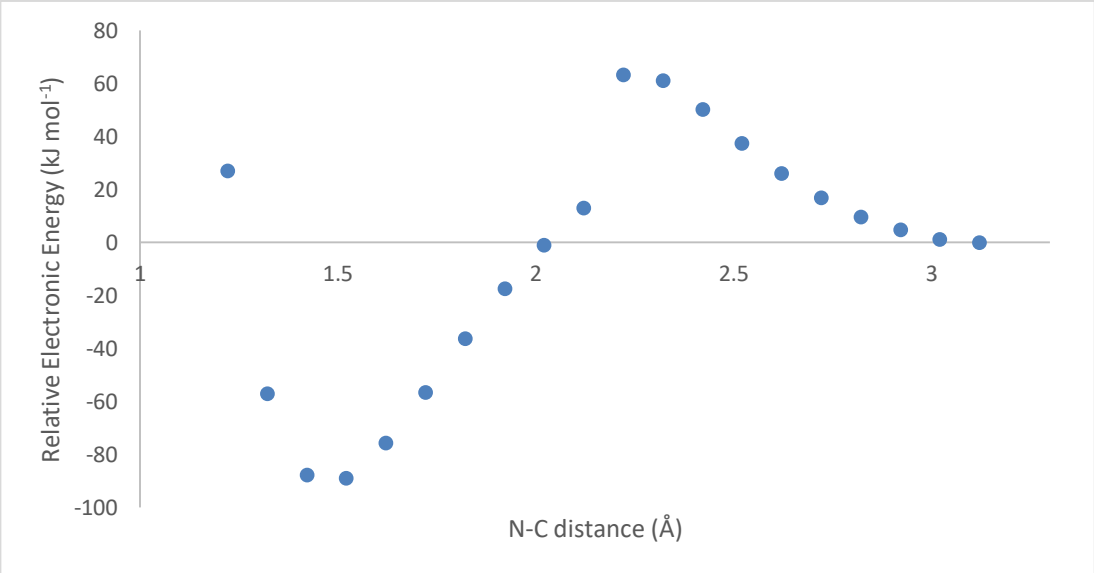


Figure S4: Relaxed PES scan of the N-C distance, 1.22 to 3.12 Å, in **4c** at the (RI)-BP86/SV(P) level.

4c O-C distance scan

Table S7: Relative electronic energies of the relaxed PES scan of the O-C distance, 1.34 to 2.84 Å, in **4c** at the (RI)-BP86/SV(P) level

O-C distance (Å)	Relative Electronic Energy (kJ mol^{-1})
2.84	0
2.74	1
2.64	4
2.54	10
2.44	18
2.34	30
2.24	47
2.14	67
2.04	-3
1.94	-17
1.84	-26
1.74	-37
1.64	-49
1.54	-59
1.44	-60
1.34	-41

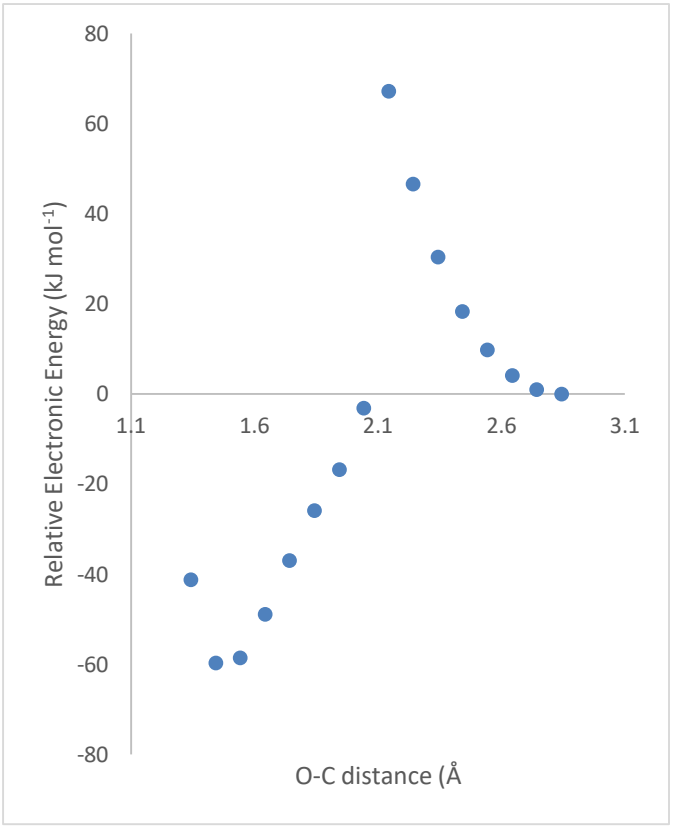


Figure S5: Relaxed PES scan of the O-C distance, 1.34 to 2.84 Å, in **4c** at the (RI)-BP86/SV(P) level.

4a O-C scan

Table S8: Relative electronic energies of the relaxed PES scan of the O-C distance, 1.70 to 2.70 Å, in **4a** at the (RI)-BP86/SV(P) level

O-C distance (Å)	Relative Electronic Energy (kJ mol^{-1})
2.70	46
2.60	46
2.50	46
2.40	47
2.30	46
2.20	45
2.10	42
2.00	37
1.90	22
1.80	12
1.70	0

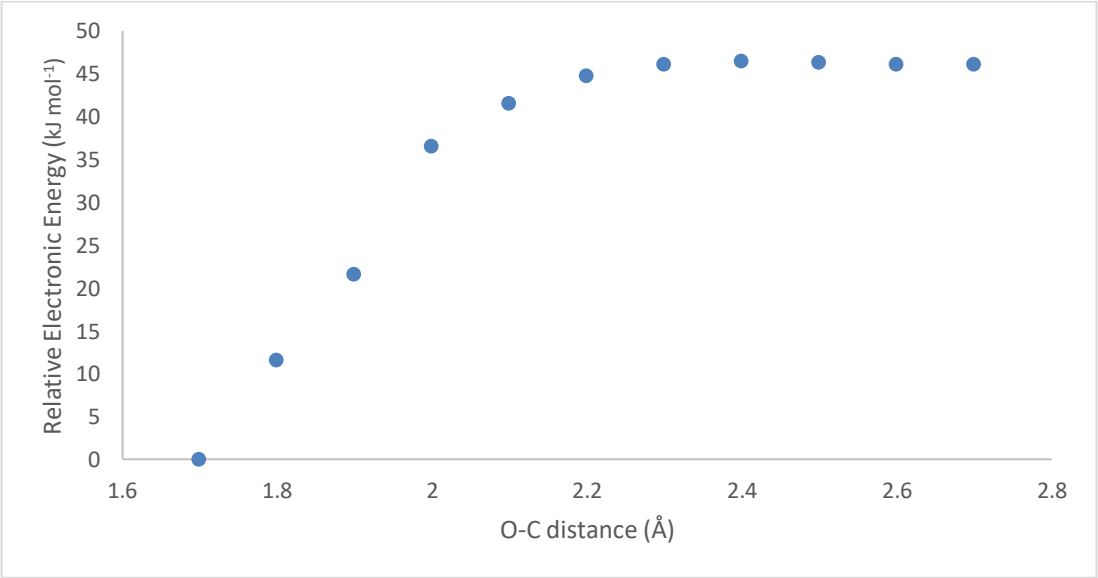
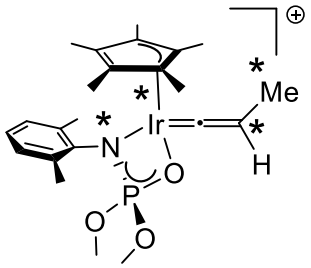


Figure S6: Relaxed PES scan of the O-C distance, 1.70 to 2.70 Å, in **4a** at the (RI)-BP86/SV(P) level.

6. PES scan of vinylidene rotation in 4c

A scan of the dihedral angle of the vinylidene in **4c** was carried out to determine the barrier of rotation around the Ir=C bond. This was carried out in TURBOMOLE by freezing the dihedral angle (N-Ir-C_β-C(Me)) during a constrained geometry optimisation. The angle was varied from 0 to 180° at 10° increments. The (RI)-BP86/SV(P) level was used for geometry optimisations, and these were subsequently followed by single point calculations at the (RI)-PBE0/def2-TZVPP level. These data suggest a low-energy barrier to rotation around the Ir=C bond of around 10 kJ mol^{-1}.



4c

Figure S7: A scan of the dihedral angle (atoms indicated by *) was carried out to determine the barrier for vinylidene rotation.

Table S9: Relative electronic energies of the relaxed PES scan of the N-Ir-C_β-C(Me) dihedral angle in **4c** at the (RI)-PBE0/def2-TZVPP//(RI)-BP86/SV(P) level

SCF Energy (a.u.)	Relative Energy (kJ mol^{-1})
-1623.6566296740	5
-1623.6569847520	4
-1623.6573345090	3
-1623.6585343700	0
-1623.6586111850	0
-1623.6583546720	1
-1623.6576142960	3
-1623.6564448280	6
-1623.6556066750	8
-1623.6549515450	10
-1623.6560821280	7
-1623.6572522610	4
-1623.6581707710	1
-1623.6586298980	0
-1623.6586115920	0
-1623.6581886720	1
-1623.6574756620	3
-1623.6569172630	4
-1623.6571636740	4

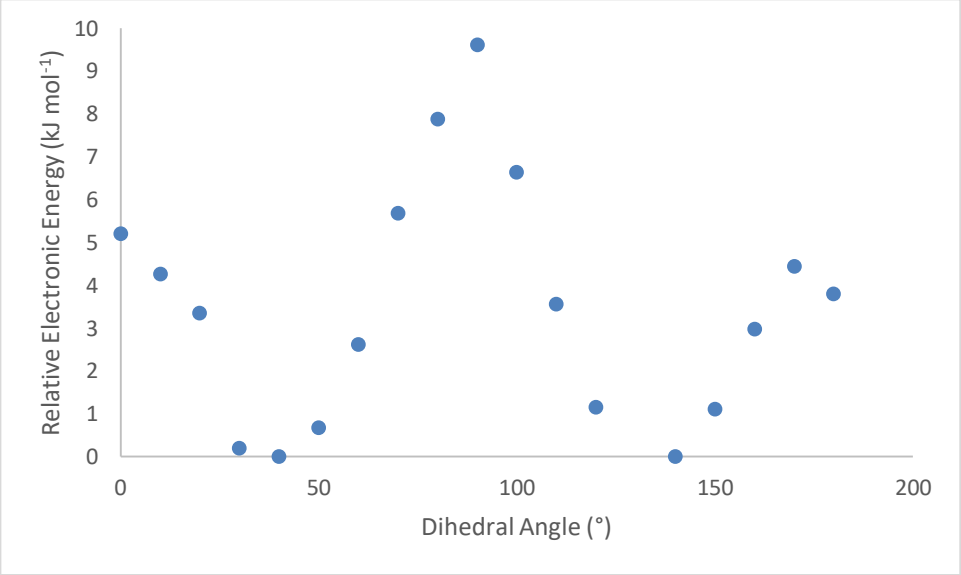


Figure S8: Relaxed PES scan of the N-Ir-C_β-C(Me) dihedral angle in **4c** at the (RI)-PBE0/def2-TZVPP level

7. Energies and vibrational spectra

2_i

BP86/SV(P) energy (au): -1622.1082370230

PBE0/def2-TZVPP energy (au): -1621.877891684
Cosmo dcm Total energy + OC corr.: -1621.9315055304

Zero point energy (au): 0.5072169
Entropy (kJ mol^{-1} K^{-1}): 0.93979
Chemical potential (kJ mol^{-1}): 1151.89

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
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2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	14.97	0.07844	YES YES
8	a	31.16	0.02324	YES YES
9	a	44.39	0.23751	YES YES
10	a	60.62	0.11746	YES YES
11	a	65.46	0.14924	YES YES
12	a	67.93	1.45831	YES YES
13	a	73.77	2.90436	YES YES
14	a	83.88	2.17351	YES YES
15	a	95.75	0.18166	YES YES
16	a	98.84	0.68415	YES YES
17	a	100.35	0.62338	YES YES
18	a	102.15	0.17296	YES YES
19	a	109.89	1.07694	YES YES
20	a	110.71	0.42161	YES YES
21	a	115.79	0.80004	YES YES
22	a	123.12	0.05476	YES YES
23	a	130.18	0.35106	YES YES
24	a	133.47	1.46811	YES YES
25	a	137.35	0.43692	YES YES
26	a	139.87	0.14971	YES YES
27	a	146.56	0.28245	YES YES
28	a	151.79	0.41098	YES YES
29	a	155.60	1.41114	YES YES
30	a	164.36	2.89636	YES YES

31	a	165.75	1.42469	YES	YES
32	a	168.78	1.68675	YES	YES
33	a	172.23	1.58178	YES	YES
34	a	178.13	0.89630	YES	YES
35	a	181.96	6.57035	YES	YES
36	a	191.60	11.65040	YES	YES
37	a	201.95	3.97739	YES	YES
38	a	212.87	1.37857	YES	YES
39	a	220.29	5.88225	YES	YES
40	a	229.85	2.94312	YES	YES
41	a	230.34	2.03710	YES	YES
42	a	265.41	28.08120	YES	YES
43	a	277.18	2.02718	YES	YES
44	a	288.71	7.80789	YES	YES
45	a	290.54	12.02080	YES	YES
46	a	293.96	2.66961	YES	YES
47	a	299.75	7.20644	YES	YES
48	a	313.19	9.44523	YES	YES
49	a	320.97	0.28856	YES	YES
50	a	330.12	5.09498	YES	YES

2_{ii}

BP86/SV(P) energy (au): -1622.1082121780

PBE0/def2-TZVPP energy (au): -1621.877851929
Cosmo dcm Total energy + OC corr.: -1621.9314130491

Zero point energy (au): 0.5070843
Entropy (kJ mol^{-1} K^{-1}): 0.94632
Chemical potential (kJ mol^{-1}): 1149.75

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
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2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	8.20	0.07705	YES YES
8	a	30.36	0.02570	YES YES
9	a	43.82	0.21529	YES YES
10	a	60.31	0.07059	YES YES
11	a	65.68	0.13264	YES YES
12	a	67.52	1.65193	YES YES
13	a	73.38	2.77065	YES YES
14	a	82.87	2.20172	YES YES
15	a	94.85	0.14998	YES YES
16	a	97.93	0.66571	YES YES
17	a	99.79	0.52980	YES YES
18	a	101.56	0.23251	YES YES
19	a	109.13	0.94911	YES YES
20	a	110.21	0.47464	YES YES
21	a	120.72	0.25507	YES YES
22	a	121.64	0.53491	YES YES
23	a	129.75	0.44419	YES YES
24	a	133.41	1.64864	YES YES
25	a	134.66	0.12391	YES YES
26	a	137.51	0.41972	YES YES
27	a	146.53	0.44141	YES YES
28	a	150.99	0.44542	YES YES
29	a	155.72	1.33499	YES YES
30	a	160.86	0.51462	YES YES
31	a	164.12	1.85363	YES YES
32	a	167.77	3.98707	YES YES
33	a	170.74	1.11002	YES YES

34	a	179.57	1.63271	YES	YES
35	a	182.32	5.79004	YES	YES
36	a	191.65	11.22989	YES	YES
37	a	201.94	4.03771	YES	YES
38	a	212.92	1.45995	YES	YES
39	a	219.88	5.83240	YES	YES
40	a	228.63	0.79054	YES	YES
41	a	229.98	4.22905	YES	YES
42	a	265.14	27.88963	YES	YES
43	a	278.54	1.43092	YES	YES
44	a	288.68	9.22514	YES	YES
45	a	289.88	11.43374	YES	YES
46	a	292.47	2.94411	YES	YES
47	a	299.19	7.33027	YES	YES
48	a	311.73	8.83795	YES	YES
49	a	320.41	0.41008	YES	YES
50	a	330.43	4.84499	YES	YES

2_{iii}

BP86/SV(P) energy (au): -1622.1057225070

PBE0/def2-TZVPP energy (au): -1621.876070569
Cosmo dcm Total energy + OC corr.: -1621.9309055670

Zero point energy (au): 0.5068546
Entropy (kJ mol^{-1} K^{-1}): 0.94839
Chemical potential (kJ mol^{-1}): 1148.97

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
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2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	15.59	0.08067	YES YES
8	a	24.44	0.13295	YES YES
9	a	44.67	0.32469	YES YES
10	a	60.90	0.33578	YES YES
11	a	62.99	0.18363	YES YES
12	a	68.63	1.04331	YES YES
13	a	70.92	2.57529	YES YES
14	a	82.57	0.57091	YES YES
15	a	83.10	0.98744	YES YES
16	a	89.04	2.14620	YES YES
17	a	95.02	0.39763	YES YES
18	a	102.16	0.70776	YES YES
19	a	105.03	0.72868	YES YES
20	a	107.55	0.82348	YES YES
21	a	110.22	0.66356	YES YES
22	a	123.70	0.80793	YES YES
23	a	126.41	1.69501	YES YES
24	a	127.62	0.71902	YES YES
25	a	134.77	0.70509	YES YES
26	a	140.96	0.15773	YES YES
27	a	143.92	0.01953	YES YES
28	a	146.24	0.27076	YES YES
29	a	150.30	1.36576	YES YES
30	a	155.82	0.18750	YES YES
31	a	164.77	0.67596	YES YES
32	a	166.76	1.50850	YES YES
33	a	169.10	1.78940	YES YES

34	a	180.85	2.88659	YES	YES
35	a	182.40	3.98724	YES	YES
36	a	194.68	8.55150	YES	YES
37	a	203.06	3.11493	YES	YES
38	a	209.10	2.29040	YES	YES
39	a	219.18	8.98620	YES	YES
40	a	227.49	4.82748	YES	YES
41	a	231.26	0.33461	YES	YES
42	a	261.71	24.68260	YES	YES
43	a	272.17	1.61978	YES	YES
44	a	286.77	0.73879	YES	YES
45	a	290.92	3.39992	YES	YES
46	a	293.33	11.59252	YES	YES
47	a	305.90	18.16421	YES	YES
48	a	314.32	5.71570	YES	YES
49	a	318.36	0.91473	YES	YES
50	a	324.21	5.01391	YES	YES

2_{iv}

BP86/SV(P) energy (au): -1622.0984765710

PBE0/def2-TZVPP energy (au): -1621.871852997
Cosmo dcm Total energy + OC corr.: -1621.9241572125

Zero point energy (au): 0.5091124
Entropy (kJ mol^{-1} K^{-1}): 0.91342
Chemical potential (kJ mol^{-1}): 1162.23

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
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3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	22.56	0.07447	YES YES
8	a	35.08	0.23678	YES YES
9	a	46.23	0.26392	YES YES
10	a	53.33	0.58471	YES YES
11	a	57.24	1.04394	YES YES
12	a	63.97	0.75173	YES YES
13	a	82.35	1.18172	YES YES
14	a	86.41	0.20854	YES YES
15	a	89.49	0.48607	YES YES
16	a	91.96	0.19186	YES YES
17	a	101.50	1.06495	YES YES
18	a	107.51	1.18303	YES YES
19	a	113.20	1.26720	YES YES
20	a	120.41	0.29169	YES YES
21	a	127.77	1.50603	YES YES
22	a	131.34	4.07672	YES YES
23	a	133.59	0.19749	YES YES
24	a	147.12	2.97344	YES YES
25	a	161.28	1.86884	YES YES
26	a	164.28	2.03792	YES YES
27	a	173.33	2.39454	YES YES
28	a	176.75	3.81944	YES YES
29	a	179.96	2.73068	YES YES
30	a	182.30	2.04223	YES YES
31	a	185.85	2.05532	YES YES
32	a	189.04	0.64815	YES YES

33	a	198.91	1.91306	YES	YES
34	a	206.87	1.42460	YES	YES
35	a	212.15	1.63472	YES	YES
36	a	216.46	1.16219	YES	YES
37	a	230.45	2.84728	YES	YES
38	a	234.96	0.73504	YES	YES
39	a	243.87	2.29109	YES	YES
40	a	256.82	1.52548	YES	YES
41	a	269.30	4.17457	YES	YES
42	a	277.64	0.04098	YES	YES
43	a	284.83	4.41686	YES	YES
44	a	294.32	0.41317	YES	YES
45	a	295.71	4.42291	YES	YES
46	a	303.08	3.45125	YES	YES
47	a	305.09	24.58896	YES	YES
48	a	333.01	2.49981	YES	YES
49	a	346.08	4.68851	YES	YES
50	a	347.58	19.73730	YES	YES

2_v

BP86/SV(P) energy (au): -1622.1042998730

PBE0/def2-TZVPP energy (au): -1621.879828203
Cosmo dcm Total energy + OC corr.: -1621.9310521919

Zero point energy (au): 0.5079000
Entropy (kJ mol^{-1} K^{-1}): 0.93826
Chemical potential (kJ mol^{-1}): 1153.36

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
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2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	14.77	0.08158	YES YES
8	a	33.94	0.22021	YES YES
9	a	34.90	0.20878	YES YES
10	a	47.52	0.19101	YES YES
11	a	55.90	1.65127	YES YES
12	a	59.99	0.43562	YES YES
13	a	67.85	0.34938	YES YES
14	a	74.75	0.89226	YES YES
15	a	83.68	0.82130	YES YES
16	a	88.15	0.30471	YES YES
17	a	93.35	0.83408	YES YES
18	a	96.83	0.87990	YES YES
19	a	105.21	0.26497	YES YES
20	a	111.54	0.54371	YES YES
21	a	122.69	3.68937	YES YES
22	a	132.80	1.30101	YES YES
23	a	135.04	0.59306	YES YES
24	a	137.19	3.13307	YES YES
25	a	141.64	0.63008	YES YES
26	a	153.84	3.14710	YES YES
27	a	157.01	2.06677	YES YES
28	a	161.86	1.77101	YES YES
29	a	168.08	0.64669	YES YES
30	a	169.46	0.84789	YES YES
31	a	176.71	2.63216	YES YES
32	a	179.63	2.07675	YES YES
33	a	182.34	1.46024	YES YES

34	a	191.89	1.70553	YES	YES
35	a	202.94	2.85736	YES	YES
36	a	209.74	1.55702	YES	YES
37	a	217.46	19.72074	YES	YES
38	a	227.87	0.28459	YES	YES
39	a	238.67	1.31947	YES	YES
40	a	251.75	1.18515	YES	YES
41	a	263.61	3.23770	YES	YES
42	a	273.72	2.37209	YES	YES
43	a	275.10	0.35839	YES	YES
44	a	289.79	13.22509	YES	YES
45	a	290.83	9.12505	YES	YES
46	a	297.03	4.09698	YES	YES
47	a	308.74	8.18844	YES	YES
48	a	315.24	12.93948	YES	YES
49	a	338.67	7.34976	YES	YES
50	a	347.64	4.24583	YES	YES

7.1. O-Protonation Pathway

TS_{23a}

BP86/SV(P) energy (au): -1622.0932769810

PBE0/def2-TZVPP energy (au): -1621.861277162
Cosmo dcm Total energy + OC corr.: -1621.9140923088

Zero point energy (au): 0.5009151
Entropy (kJ mol^{-1} K^{-1}): 0.94374
Chemical potential (kJ mol^{-1}): 1142.07

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-55.66	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.00000	- -
8	a	14.92	0.10227	YES YES
9	a	22.76	0.22063	YES YES
10	a	34.94	1.76614	YES YES
11	a	45.39	2.04701	YES YES
12	a	50.69	1.66572	YES YES
13	a	54.03	2.73083	YES YES
14	a	61.13	0.60164	YES YES
15	a	70.26	0.61601	YES YES
16	a	72.75	1.16316	YES YES
17	a	93.54	0.18463	YES YES
18	a	103.10	0.91435	YES YES
19	a	105.45	0.02950	YES YES
20	a	112.42	0.23841	YES YES
21	a	115.19	0.49460	YES YES
22	a	121.28	1.04145	YES YES
23	a	128.76	0.34517	YES YES
24	a	129.40	0.18714	YES YES
25	a	132.45	6.31240	YES YES
26	a	133.59	1.47006	YES YES
27	a	134.51	0.70377	YES YES
28	a	136.35	2.06033	YES YES
29	a	147.99	2.35508	YES YES
30	a	153.53	2.01828	YES YES
31	a	158.41	2.05470	YES YES

32	a	161.62	4.38848	YES	YES
33	a	173.11	0.18873	YES	YES
34	a	179.86	1.98005	YES	YES
35	a	185.57	7.73683	YES	YES
36	a	194.50	9.33808	YES	YES
37	a	200.82	2.72321	YES	YES
38	a	212.48	6.84140	YES	YES
39	a	222.92	36.29272	YES	YES
40	a	228.67	0.15643	YES	YES
41	a	242.45	2.58542	YES	YES
42	a	263.46	25.21913	YES	YES
43	a	275.15	0.13926	YES	YES
44	a	291.23	0.37863	YES	YES
45	a	296.24	0.92199	YES	YES
46	a	296.97	1.69898	YES	YES
47	a	298.07	1.00736	YES	YES
48	a	308.39	13.48626	YES	YES
49	a	322.08	0.77423	YES	YES
50	a	353.08	47.45867	YES	YES

3_a

BP86/SV(P) energy (au): -1622.1137234830

PBE0/def2-TZVPP energy (au): -1621.895649288
Cosmo dcm Total energy + OC corr.: -1621.9438768378

Zero point energy (au): 0.5070737
Entropy (kJ mol^{-1} K^{-1}): 0.95917
Chemical potential (kJ mol^{-1}): 1145.90

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	15.50	0.00668	YES YES
8	a	22.00	0.09492	YES YES
9	a	32.09	0.06969	YES YES
10	a	41.82	0.15959	YES YES
11	a	46.99	1.42747	YES YES
12	a	55.58	0.19024	YES YES
13	a	62.53	1.20326	YES YES
14	a	65.26	1.71598	YES YES
15	a	70.09	0.02581	YES YES
16	a	74.94	1.89054	YES YES
17	a	85.35	0.66845	YES YES
18	a	96.78	3.00710	YES YES
19	a	105.28	1.68339	YES YES
20	a	111.71	0.10737	YES YES
21	a	120.51	0.36316	YES YES
22	a	122.76	0.35697	YES YES
23	a	124.13	0.47682	YES YES
24	a	133.02	0.20722	YES YES
25	a	136.96	2.09410	YES YES
26	a	137.18	0.29283	YES YES
27	a	139.97	0.10793	YES YES
28	a	149.97	0.22527	YES YES
29	a	152.26	2.13828	YES YES
30	a	157.97	4.07602	YES YES
31	a	161.26	3.58321	YES YES
32	a	162.75	9.05201	YES YES
33	a	167.64	0.34158	YES YES

34	a	182.51	2.86424	YES	YES
35	a	184.03	1.88743	YES	YES
36	a	195.63	0.37149	YES	YES
37	a	210.53	0.80578	YES	YES
38	a	212.81	2.55450	YES	YES
39	a	225.43	0.32640	YES	YES
40	a	246.83	4.39340	YES	YES
41	a	267.10	16.01616	YES	YES
42	a	284.92	0.42156	YES	YES
43	a	286.87	0.16430	YES	YES
44	a	290.21	0.03435	YES	YES
45	a	294.59	0.67747	YES	YES
46	a	295.19	3.81158	YES	YES
47	a	307.49	20.79146	YES	YES
48	a	322.54	0.32769	YES	YES
49	a	343.55	3.54971	YES	YES
50	a	364.23	8.82845	YES	YES

TS_{3a4}

BP86/SV(P) energy (au): -1622.1053939820

PBE0/def2-TZVPP energy (au): -1621.875032694
Cosmo dcm Total energy + OC corr.: -1621.9253873869

Zero point energy (au): 0.5041016
Entropy (kJ mol^{-1} K^{-1}): 0.93567
Chemical potential (kJ mol^{-1}): 1131.82

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-218.58	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.00000	- -
8	a	18.00	0.01351	YES YES
9	a	24.83	0.00984	YES YES
10	a	44.26	0.76396	YES YES
11	a	47.27	0.86884	YES YES
12	a	57.58	0.34768	YES YES
13	a	63.89	1.48316	YES YES
14	a	71.03	1.61902	YES YES
15	a	78.31	1.66361	YES YES
16	a	84.39	0.37472	YES YES
17	a	86.03	0.49888	YES YES
18	a	88.65	0.11128	YES YES
19	a	105.92	6.01010	YES YES
20	a	110.18	0.57925	YES YES
21	a	116.66	0.40897	YES YES
22	a	118.70	0.49334	YES YES
23	a	125.31	0.98965	YES YES
24	a	128.80	1.15645	YES YES
25	a	138.15	0.48300	YES YES
26	a	138.77	0.39506	YES YES
27	a	143.19	0.36260	YES YES
28	a	145.65	0.52807	YES YES
29	a	147.80	0.70923	YES YES
30	a	154.10	2.60813	YES YES
31	a	155.75	3.78785	YES YES
32	a	159.28	5.06072	YES YES
33	a	165.53	1.48124	YES YES

34	a	175.49	1.61533	YES	YES
35	a	187.70	5.98826	YES	YES
36	a	194.58	5.34382	YES	YES
37	a	209.68	3.03918	YES	YES
38	a	211.34	3.23015	YES	YES
39	a	224.70	0.14185	YES	YES
40	a	250.33	3.38086	YES	YES
41	a	259.15	12.80110	YES	YES
42	a	283.49	70.35905	YES	YES
43	a	288.34	2.32636	YES	YES
44	a	289.91	0.36319	YES	YES
45	a	292.49	3.63931	YES	YES
46	a	296.31	32.22341	YES	YES
47	a	302.89	16.57008	YES	YES
48	a	323.69	4.12955	YES	YES
49	a	347.24	10.21182	YES	YES
50	a	355.13	4.58532	YES	YES

4ci

BP86/SV(P) energy (au): -1622.113136054

PBE0/def2-TZVPP energy (au): -1621.88257916
Cosmo dcm Total energy + OC corr.: -1621.9331978192

Zero point energy (au): 0.5084942
Entropy (kJ mol^{-1} K^{-1}): 0.94003
Chemical potential (kJ mol^{-1}): 1154.07

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	18.98	0.12161	YES YES
8	a	25.20	0.05306	YES YES
9	a	37.33	0.16782	YES YES
10	a	46.86	0.20390	YES YES
11	a	55.82	1.88882	YES YES
12	a	60.10	0.55496	YES YES
13	a	66.52	3.20153	YES YES
14	a	71.92	1.23833	YES YES
15	a	81.40	1.80185	YES YES
16	a	90.75	0.49300	YES YES
17	a	92.41	1.24345	YES YES
18	a	102.25	0.37031	YES YES
19	a	108.97	0.65466	YES YES
20	a	109.90	0.70710	YES YES
21	a	112.76	1.68154	YES YES
22	a	122.15	1.45776	YES YES
23	a	131.70	2.39718	YES YES
24	a	138.17	0.61991	YES YES
25	a	140.85	0.43825	YES YES
26	a	149.30	1.55636	YES YES
27	a	149.88	0.56750	YES YES
28	a	155.93	0.10806	YES YES
29	a	160.50	0.73513	YES YES
30	a	163.55	0.84615	YES YES
31	a	168.10	4.79532	YES YES
32	a	169.01	0.60133	YES YES
33	a	175.06	1.94865	YES YES

34	a	185.32	0.68972	YES	YES
35	a	188.11	2.92719	YES	YES
36	a	194.92	1.42568	YES	YES
37	a	212.90	5.00974	YES	YES
38	a	219.99	0.36212	YES	YES
39	a	232.74	8.08461	YES	YES
40	a	242.26	0.42164	YES	YES
41	a	260.15	4.62049	YES	YES
42	a	269.12	1.09358	YES	YES
43	a	280.11	7.58254	YES	YES
44	a	284.99	5.52989	YES	YES
45	a	289.38	0.59908	YES	YES
46	a	295.53	2.16034	YES	YES
47	a	299.63	10.18285	YES	YES
48	a	338.87	0.26398	YES	YES
49	a	343.86	15.28672	YES	YES
50	a	375.47	28.08368	YES	YES

4cii

BP86/SV(P) energy (au): -1622.1143256180

PBE0/def2-TZVPP energy (au): -1621.883920945
Cosmo dcm Total energy + OC corr.: -1621.9345633380

Zero point energy (au): 0.5088221
Entropy (kJ mol^{-1} K^{-1}): 0.93609
Chemical potential (kJ mol^{-1}): 1155.76

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	21.17	0.08977	YES YES
8	a	28.37	0.16314	YES YES
9	a	35.15	0.31169	YES YES
10	a	45.82	0.42924	YES YES
11	a	54.15	0.98756	YES YES
12	a	58.79	0.46038	YES YES
13	a	62.68	3.68329	YES YES
14	a	68.09	3.10938	YES YES
15	a	81.46	0.95862	YES YES
16	a	85.86	0.70253	YES YES
17	a	95.40	1.28040	YES YES
18	a	102.85	0.60175	YES YES
19	a	108.63	0.82178	YES YES
20	a	122.18	1.31478	YES YES
21	a	123.65	0.20901	YES YES
22	a	131.40	2.26051	YES YES
23	a	132.69	0.70502	YES YES
24	a	144.40	0.89325	YES YES
25	a	145.52	1.37044	YES YES
26	a	150.15	0.26992	YES YES
27	a	153.01	0.37548	YES YES
28	a	157.00	1.22394	YES YES
29	a	160.74	1.09216	YES YES
30	a	164.82	1.14810	YES YES
31	a	171.60	0.39744	YES YES
32	a	175.84	5.20375	YES YES
33	a	179.64	0.30008	YES YES

34	a	182.28	1.71493	YES	YES
35	a	184.44	0.40637	YES	YES
36	a	197.91	2.41503	YES	YES
37	a	207.05	6.81793	YES	YES
38	a	213.88	0.42505	YES	YES
39	a	232.49	7.56675	YES	YES
40	a	243.25	2.31892	YES	YES
41	a	262.95	5.69254	YES	YES
42	a	269.91	1.31702	YES	YES
43	a	280.07	10.21470	YES	YES
44	a	284.50	4.74108	YES	YES
45	a	291.55	0.92087	YES	YES
46	a	299.44	0.71728	YES	YES
47	a	301.44	6.79303	YES	YES
48	a	336.47	0.15611	YES	YES
49	a	342.34	14.79030	YES	YES
50	a	374.58	27.05682	YES	YES

4ai

BP86/SV(P) energy (au): -1622.1057

PBE0/def2-TZVPP energy (au): -1621.86989194
Cosmo dcm Total energy + OC corr.: -1621.9270841217

Zero point energy (au): 0.5075798
Entropy (kJ mol^{-1} K^{-1}): 0.9549
Chemical potential (kJ mol^{-1}): 1129.89

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	14.50	0.28700	YES YES
8	a	22.62	0.48153	YES YES
9	a	27.00	0.64150	YES YES
10	a	53.19	0.92797	YES YES
11	a	55.01	0.78138	YES YES
12	a	58.35	1.04200	YES YES
13	a	67.64	2.10817	YES YES
14	a	68.92	0.47813	YES YES
15	a	76.10	0.26155	YES YES
16	a	80.33	1.03989	YES YES
17	a	90.43	0.11817	YES YES
18	a	101.31	1.34395	YES YES
19	a	107.45	1.51268	YES YES
20	a	111.44	0.10174	YES YES
21	a	115.82	2.67845	YES YES
22	a	125.42	0.17392	YES YES
23	a	127.87	0.31956	YES YES
24	a	130.23	4.81626	YES YES
25	a	133.68	0.14069	YES YES
26	a	138.47	2.16924	YES YES
27	a	143.33	1.04228	YES YES
28	a	145.08	0.16215	YES YES
29	a	147.53	1.58065	YES YES
30	a	154.96	0.39043	YES YES
31	a	160.33	2.48893	YES YES

32	a	161.15	4.35076	YES	YES
33	a	171.54	0.66145	YES	YES
34	a	178.12	3.09857	YES	YES
35	a	184.09	3.39363	YES	YES
36	a	189.38	2.83429	YES	YES
37	a	205.42	2.46492	YES	YES
38	a	215.47	9.82617	YES	YES
39	a	227.97	0.32999	YES	YES
40	a	232.42	1.67702	YES	YES
41	a	245.24	10.70866	YES	YES
42	a	270.49	15.31352	YES	YES
43	a	277.81	0.13125	YES	YES
44	a	286.67	0.40115	YES	YES
45	a	288.34	2.16044	YES	YES
46	a	291.85	0.15758	YES	YES
47	a	301.47	16.69310	YES	YES
48	a	324.38	2.98596	YES	YES
49	a	345.43	13.23498	YES	YES
50	a	356.71	2.95068	YES	YES

4aii

BP86/SV(P) energy (au): -1622.1059740070

PBE0/def2-TZVPP energy (au): -1621.870008155
Cosmo dcm Total energy + OC corr.: -1621.9269661362

Zero point energy (au): 0.5076509
Entropy (kJ mol^{-1} K^{-1}): 0.95034
Chemical potential (kJ mol^{-1}): 1149.88

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	23.03	0.06941	YES YES
8	a	23.52	0.46607	YES YES
9	a	35.36	0.03888	YES YES
10	a	52.57	1.23854	YES YES
11	a	55.99	0.56683	YES YES
12	a	59.84	0.86582	YES YES
13	a	66.02	2.58926	YES YES
14	a	69.48	0.66326	YES YES
15	a	79.92	0.24839	YES YES
16	a	85.62	0.71788	YES YES
17	a	91.83	0.76344	YES YES
18	a	96.86	0.24224	YES YES
19	a	101.85	0.92270	YES YES
20	a	106.55	0.62593	YES YES
21	a	114.32	0.18180	YES YES
22	a	119.97	3.41792	YES YES
23	a	123.07	0.79597	YES YES
24	a	128.16	2.63900	YES YES
25	a	132.23	0.03668	YES YES
26	a	137.86	1.11242	YES YES
27	a	144.28	0.28673	YES YES
28	a	149.00	0.02160	YES YES
29	a	150.15	0.17167	YES YES
30	a	154.75	1.25468	YES YES
31	a	157.26	5.56259	YES YES
32	a	158.46	1.04724	YES YES
33	a	171.65	1.45314	YES YES

34	a	177.67	2.25953	YES	YES
35	a	182.45	4.03349	YES	YES
36	a	183.79	0.76589	YES	YES
37	a	192.48	7.41734	YES	YES
38	a	209.76	3.95237	YES	YES
39	a	223.78	1.30342	YES	YES
40	a	227.04	0.32271	YES	YES
41	a	238.42	6.61098	YES	YES
42	a	263.17	20.84572	YES	YES
43	a	277.00	0.27155	YES	YES
44	a	286.98	0.40075	YES	YES
45	a	289.11	1.40736	YES	YES
46	a	292.46	0.77644	YES	YES
47	a	301.74	17.79130	YES	YES
48	a	323.55	2.51157	YES	YES
49	a	340.31	10.58949	YES	YES
50	a	371.28	2.31230	YES	YES

4b

BP86/SV(P) energy (au): -1622.0795120740

PBE0/def2-TZVPP energy (au): -1621.835227614
Cosmo dcm Total energy + OC corr.: -1621.8898089778

Zero point energy (au): 0.5064754
Entropy (kJ mol^{-1} K^{-1}): 0.98689
Chemical potential (kJ mol^{-1}): 1137.40

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	11.26	0.01189	YES YES
8	a	20.19	0.22846	YES YES
9	a	21.39	0.40105	YES YES
10	a	28.20	0.16290	YES YES
11	a	41.51	0.80657	YES YES
12	a	48.45	2.75126	YES YES
13	a	51.34	0.44847	YES YES
14	a	51.97	2.17679	YES YES
15	a	63.42	0.65884	YES YES
16	a	66.29	3.77064	YES YES
17	a	85.93	1.13446	YES YES
18	a	90.35	5.57201	YES YES
19	a	95.16	1.76038	YES YES
20	a	102.07	4.46134	YES YES
21	a	109.05	9.01880	YES YES
22	a	120.10	1.07361	YES YES
23	a	123.06	2.38716	YES YES
24	a	134.23	0.17422	YES YES
25	a	135.53	0.16440	YES YES
26	a	137.24	0.21118	YES YES
27	a	139.85	0.67495	YES YES
28	a	144.24	2.96464	YES YES
29	a	149.65	0.31819	YES YES
30	a	151.24	0.90929	YES YES
31	a	152.41	0.78962	YES YES
32	a	157.55	2.14878	YES YES
33	a	159.34	1.99425	YES YES

34	a	168.83	0.07479	YES	YES
35	a	171.22	0.13959	YES	YES
36	a	184.22	2.61615	YES	YES
37	a	189.08	5.64502	YES	YES
38	a	195.06	1.31387	YES	YES
39	a	220.02	0.75328	YES	YES
40	a	221.93	0.08720	YES	YES
41	a	249.21	5.08029	YES	YES
42	a	271.27	6.70231	YES	YES
43	a	284.54	0.04688	YES	YES
44	a	286.38	0.07398	YES	YES
45	a	290.28	0.21584	YES	YES
46	a	294.99	0.75890	YES	YES
47	a	304.66	4.25223	YES	YES
48	a	326.14	3.09408	YES	YES
49	a	340.71	4.22919	YES	YES
50	a	357.10	35.32707	YES	YES

5_a_E

BP86/SV(P) energy (au): -1622.1464442500

PBE0/def2-TZVPP energy (au): -1621.918632324
Cosmo dcm Total energy + OC corr.: -1621.9668937253

Zero point energy (au): 0.5106270
Entropy (kJ mol^{-1} K^{-1}): 0.93154
Chemical potential (kJ mol^{-1}): 1160.65

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	14.07	0.02536	YES YES
8	a	22.47	0.18118	YES YES
9	a	42.26	0.60989	YES YES
10	a	50.25	0.13830	YES YES
11	a	55.29	1.12592	YES YES
12	a	56.50	0.40670	YES YES
13	a	67.73	1.70711	YES YES
14	a	68.63	1.17799	YES YES
15	a	85.47	0.96007	YES YES
16	a	93.87	1.45333	YES YES
17	a	98.13	0.37442	YES YES
18	a	105.82	1.96359	YES YES
19	a	109.67	0.43353	YES YES
20	a	114.10	0.33782	YES YES
21	a	118.99	0.65107	YES YES
22	a	129.73	0.35443	YES YES
23	a	137.83	2.20315	YES YES
24	a	139.36	0.59559	YES YES
25	a	143.39	1.67783	YES YES
26	a	144.50	0.41065	YES YES
27	a	148.53	1.78602	YES YES
28	a	150.78	0.48885	YES YES
29	a	160.86	2.22569	YES YES
30	a	169.98	2.88439	YES YES
31	a	172.02	0.84912	YES YES
32	a	175.64	0.67715	YES YES
33	a	176.89	1.96354	YES YES

34	a	183.80	0.58253	YES	YES
35	a	191.50	0.72230	YES	YES
36	a	203.25	0.85491	YES	YES
37	a	206.76	2.90037	YES	YES
38	a	222.03	2.90578	YES	YES
39	a	223.63	0.74383	YES	YES
40	a	249.45	4.25155	YES	YES
41	a	282.80	0.01565	YES	YES
42	a	284.15	0.26785	YES	YES
43	a	288.94	13.02193	YES	YES
44	a	292.18	8.09606	YES	YES
45	a	293.47	0.95193	YES	YES
46	a	304.23	1.27141	YES	YES
47	a	314.79	2.37842	YES	YES
48	a	334.68	6.98106	YES	YES
49	a	368.36	3.69987	YES	YES
50	a	388.48	9.90919	YES	YES

5_a_*Z*

BP86/SV(P) energy (au): -1622.1380723270

PBE0/def2-TZVPP energy (au): -1621.910189416
Cosmo dcm Total energy + OC corr.: -1621.9586387654

Zero point energy (au): 0.5104195
Entropy (kJ mol^{-1} K^{-1}): 0.93161
Chemical potential (kJ mol^{-1}): 1160.13

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	10.17	0.04648	YES YES
8	a	29.61	0.30976	YES YES
9	a	41.21	0.16442	YES YES
10	a	44.67	0.05522	YES YES
11	a	54.53	0.21623	YES YES
12	a	59.89	1.46407	YES YES
13	a	68.74	0.01998	YES YES
14	a	77.76	4.01501	YES YES
15	a	89.32	2.36232	YES YES
16	a	96.80	0.14047	YES YES
17	a	100.92	1.25185	YES YES
18	a	105.37	0.11143	YES YES
19	a	110.71	1.39418	YES YES
20	a	112.76	0.69273	YES YES
21	a	114.55	0.09646	YES YES
22	a	123.58	1.07841	YES YES
23	a	130.64	0.18323	YES YES
24	a	134.23	0.30192	YES YES
25	a	140.08	1.56199	YES YES
26	a	145.07	1.19501	YES YES
27	a	148.66	0.27006	YES YES
28	a	151.45	0.93064	YES YES
29	a	159.98	1.72785	YES YES
30	a	162.30	0.07915	YES YES
31	a	169.31	2.17582	YES YES
32	a	182.31	0.87691	YES YES
33	a	184.22	2.29597	YES YES

34	a	193.62	4.04839	YES	YES
35	a	199.26	1.10142	YES	YES
36	a	208.92	0.90792	YES	YES
37	a	213.76	1.44557	YES	YES
38	a	224.69	0.04364	YES	YES
39	a	233.43	1.41989	YES	YES
40	a	250.64	4.00891	YES	YES
41	a	276.54	0.06210	YES	YES
42	a	280.63	0.00856	YES	YES
43	a	288.62	1.41947	YES	YES
44	a	295.34	12.37929	YES	YES
45	a	301.35	5.08713	YES	YES
46	a	307.00	4.64815	YES	YES
47	a	323.12	13.10307	YES	YES
48	a	354.62	1.37006	YES	YES
49	a	367.29	8.19076	YES	YES
50	a	381.15	10.18261	YES	YES

7.2. N-Protonation Pathway

TS_{23b}

BP86/SV(P) energy (au): -1622.0774225920

PBE0/def2-TZVPP energy (au): -1621.848621196
Cosmo dcm Total energy + OC corr.: -1621.9001203160

Zero point energy (au): 0.5050648
Entropy (kJ mol^{-1} K^{-1}): 0.95665
Chemical potential (kJ mol^{-1}): 1135.85

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-370.58	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.00000	- -
8	a	12.22	0.37561	YES YES
9	a	18.82	0.07016	YES YES
10	a	26.40	0.66685	YES YES
11	a	38.40	1.03159	YES YES
12	a	42.21	1.26866	YES YES
13	a	55.22	1.18068	YES YES
14	a	57.62	1.08564	YES YES
15	a	63.25	0.46442	YES YES
16	a	66.80	2.38506	YES YES
17	a	77.53	0.88165	YES YES
18	a	84.77	0.85462	YES YES
19	a	97.68	1.46505	YES YES
20	a	102.84	1.92011	YES YES
21	a	109.83	0.72948	YES YES
22	a	113.14	4.29965	YES YES
23	a	124.77	3.51845	YES YES
24	a	128.85	2.99551	YES YES
25	a	137.01	1.77883	YES YES
26	a	141.92	1.56311	YES YES
27	a	147.57	0.53151	YES YES
28	a	149.46	0.52269	YES YES
29	a	152.41	2.83520	YES YES
30	a	156.21	1.71710	YES YES
31	a	164.38	3.13432	YES YES

32	a	172.64	3.09210	YES	YES
33	a	183.56	4.65414	YES	YES
34	a	186.18	9.84048	YES	YES
35	a	191.51	2.02328	YES	YES
36	a	200.20	2.20442	YES	YES
37	a	211.87	0.54089	YES	YES
38	a	218.73	1.38325	YES	YES
39	a	227.02	12.56517	YES	YES
40	a	237.59	7.36538	YES	YES
41	a	242.91	3.98821	YES	YES
42	a	267.54	20.45344	YES	YES
43	a	276.54	0.55348	YES	YES
44	a	280.44	4.82990	YES	YES
45	a	284.14	0.12413	YES	YES
46	a	296.41	1.37699	YES	YES
47	a	299.42	3.79128	YES	YES
48	a	307.25	11.89826	YES	YES
49	a	333.58	85.07281	YES	YES
50	a	359.16	20.14313	YES	YES

3_b

BP86/SV(P) energy (au): -1622.1230581790

PBE0/def2-TZVPP energy (au): -1621.901981367
Cosmo dcm Total energy + OC corr.: -1621.9516693377

Zero point energy (au): 0.5079803
Entropy (kJ mol^{-1} K^{-1}): 1.01707
Chemical potential (kJ mol^{-1}): 1133.23

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	6.29	0.03234	YES YES
8	a	9.49	0.16731	YES YES
9	a	15.91	0.22635	YES YES
10	a	24.86	0.29175	YES YES
11	a	31.51	0.51914	YES YES
12	a	35.31	0.19808	YES YES
13	a	52.20	0.87284	YES YES
14	a	54.05	0.53505	YES YES
15	a	58.54	1.46311	YES YES
16	a	65.09	0.02039	YES YES
17	a	72.60	1.81801	YES YES
18	a	81.85	0.24352	YES YES
19	a	86.88	1.83554	YES YES
20	a	99.39	0.85950	YES YES
21	a	100.79	0.16610	YES YES
22	a	102.12	1.30736	YES YES
23	a	112.00	0.21376	YES YES
24	a	126.71	1.48802	YES YES
25	a	128.86	0.41862	YES YES
26	a	130.22	0.95716	YES YES
27	a	132.51	0.40344	YES YES
28	a	135.66	1.30773	YES YES
29	a	139.01	0.51186	YES YES
30	a	141.41	0.28367	YES YES
31	a	143.50	0.09269	YES YES
32	a	152.86	8.01789	YES YES
33	a	156.48	0.76347	YES YES

34	a	158.28	8.89638	YES	YES
35	a	179.24	6.39504	YES	YES
36	a	187.50	1.06030	YES	YES
37	a	208.51	3.92892	YES	YES
38	a	216.95	2.70962	YES	YES
39	a	224.17	8.83802	YES	YES
40	a	248.04	17.86742	YES	YES
41	a	254.69	3.16741	YES	YES
42	a	269.55	2.30903	YES	YES
43	a	285.05	0.23242	YES	YES
44	a	286.79	19.99747	YES	YES
45	a	289.31	3.72902	YES	YES
46	a	292.90	1.75689	YES	YES
47	a	302.06	2.66784	YES	YES
48	a	336.24	0.10645	YES	YES
49	a	340.48	10.30911	YES	YES
50	a	355.66	9.77031	YES	YES

TS_{3b5b}

BP86/SV(P) energy (au): -1622.0746159670

PBE0/def2-TZVPP energy (au): -1621.836566846
Cosmo dcm Total energy + OC corr.: -1621.8969800949

Zero point energy (au): 0.5039816
Entropy (kJ mol^{-1} K^{-1}): 0.98665
Chemical potential (kJ mol^{-1}): 1129.89

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number cm**(-1)	IR intensity km/mol	selection rules IR	RAMAN
1	a	-203.19	0.00000	YES	YES
2		0.00	0.00000	-	-
3		0.00	0.00000	-	-
4		0.00	0.00000	-	-
5		0.00	0.00000	-	-
6		0.00	0.00000	-	-
7		0.00	0.00000	-	-
8	a	10.61	0.03024	YES	YES
9	a	13.78	0.13133	YES	YES
10	a	23.34	1.38926	YES	YES
11	a	29.51	0.16911	YES	YES
12	a	34.47	0.22415	YES	YES
13	a	37.67	0.16252	YES	YES
14	a	51.49	0.34547	YES	YES
15	a	53.78	0.05634	YES	YES
16	a	59.39	1.60183	YES	YES
17	a	73.40	3.84406	YES	YES
18	a	85.27	0.28369	YES	YES
19	a	90.80	1.14884	YES	YES
20	a	101.01	1.66628	YES	YES
21	a	103.95	1.41432	YES	YES
22	a	107.57	0.95003	YES	YES
23	a	112.48	1.76051	YES	YES
24	a	114.24	0.81575	YES	YES
25	a	122.20	1.56876	YES	YES
26	a	125.69	3.33501	YES	YES
27	a	134.18	0.56828	YES	YES
28	a	137.10	3.46998	YES	YES
29	a	140.64	2.86634	YES	YES
30	a	147.14	2.29114	YES	YES
31	a	147.93	1.24357	YES	YES
32	a	151.68	0.58924	YES	YES
33	a	156.38	0.72658	YES	YES

34	a	161.21	3.80117	YES	YES
35	a	170.48	2.39263	YES	YES
36	a	188.69	5.72396	YES	YES
37	a	202.83	4.34744	YES	YES
38	a	219.80	0.19512	YES	YES
39	a	225.80	7.93635	YES	YES
40	a	230.99	4.34602	YES	YES
41	a	259.37	14.42837	YES	YES
42	a	265.25	16.22944	YES	YES
43	a	283.57	4.89450	YES	YES
44	a	284.68	7.61873	YES	YES
45	a	285.83	6.68183	YES	YES
46	a	294.11	2.08745	YES	YES
47	a	294.91	2.11635	YES	YES
48	a	312.91	82.61191	YES	YES
49	a	338.49	6.99669	YES	YES
50	a	347.42	8.91401	YES	YES

5_b_E

BP86/SV(P) energy (au): -1622.1504096830

PBE0/def2-TZVPP energy (au): -1621.922746341
Cosmo dcm Total energy + OC corr.: -1621.9712641286

Zero point energy (au): 0.5109353
Entropy (kJ mol^{-1} K^{-1}): 0.93928
Chemical potential (kJ mol^{-1}): 1159.48

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	14.59	0.08509	YES YES
8	a	21.58	0.26045	YES YES
9	a	32.83	0.59588	YES YES
10	a	50.98	1.01786	YES YES
11	a	55.65	1.04636	YES YES
12	a	65.53	0.50710	YES YES
13	a	68.90	0.55140	YES YES
14	a	72.70	0.24899	YES YES
15	a	80.68	1.79009	YES YES
16	a	86.17	0.92527	YES YES
17	a	95.39	1.14092	YES YES
18	a	99.53	1.75637	YES YES
19	a	102.97	0.02468	YES YES
20	a	105.03	0.90274	YES YES
21	a	112.79	1.85985	YES YES
22	a	118.09	0.07593	YES YES
23	a	121.28	1.08772	YES YES
24	a	124.43	1.18236	YES YES
25	a	135.14	0.86926	YES YES
26	a	141.29	0.92287	YES YES
27	a	146.23	0.47819	YES YES
28	a	148.76	1.10018	YES YES
29	a	153.50	0.15985	YES YES
30	a	160.07	1.26393	YES YES
31	a	164.17	0.30099	YES YES
32	a	170.69	1.88254	YES YES
33	a	177.10	0.79416	YES YES

34	a	185.60	0.58747	YES	YES
35	a	190.81	3.15281	YES	YES
36	a	204.47	2.05003	YES	YES
37	a	209.34	4.28214	YES	YES
38	a	221.02	0.36763	YES	YES
39	a	236.30	4.39285	YES	YES
40	a	250.54	3.93653	YES	YES
41	a	287.13	0.22726	YES	YES
42	a	293.35	0.21469	YES	YES
43	a	295.26	4.07284	YES	YES
44	a	296.45	1.11166	YES	YES
45	a	305.81	1.60478	YES	YES
46	a	309.20	7.35844	YES	YES
47	a	323.60	17.51163	YES	YES
48	a	340.71	1.38400	YES	YES
49	a	364.62	14.77865	YES	YES
50	a	383.66	11.26412	YES	YES

5_b_*Z*

BP86/SV(P) energy (au): -1622.1488115210

PBE0/def2-TZVPP energy (au): -1621.921753263
Cosmo dcm Total energy + OC corr.: -1621.9703104288

Zero point energy (au): 0.5106428
Entropy (kJ mol^{-1} K^{-1}): 0.94226
Chemical potential (kJ mol^{-1}): 1158.13

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	16.11	0.11114	YES YES
8	a	21.73	0.50063	YES YES
9	a	31.61	0.25009	YES YES
10	a	49.01	1.09454	YES YES
11	a	53.78	0.58170	YES YES
12	a	60.85	0.33364	YES YES
13	a	62.44	0.34908	YES YES
14	a	74.73	1.55047	YES YES
15	a	79.30	1.13983	YES YES
16	a	81.76	0.71733	YES YES
17	a	85.75	2.43562	YES YES
18	a	95.49	2.15319	YES YES
19	a	99.08	0.59658	YES YES
20	a	114.09	0.18551	YES YES
21	a	117.13	0.18398	YES YES
22	a	121.13	1.10655	YES YES
23	a	123.80	0.74875	YES YES
24	a	130.60	0.31012	YES YES
25	a	133.55	0.06107	YES YES
26	a	138.60	0.77949	YES YES
27	a	142.53	0.25828	YES YES
28	a	144.29	0.66827	YES YES
29	a	147.62	0.86184	YES YES
30	a	162.58	1.63555	YES YES
31	a	169.76	1.63338	YES YES
32	a	177.58	0.96690	YES YES
33	a	186.63	1.37761	YES YES

34	a	189.64	1.17040	YES	YES
35	a	199.65	3.41899	YES	YES
36	a	205.33	1.41818	YES	YES
37	a	217.16	0.00630	YES	YES
38	a	222.64	0.88687	YES	YES
39	a	228.80	7.88525	YES	YES
40	a	247.41	3.53765	YES	YES
41	a	275.57	0.25637	YES	YES
42	a	282.26	0.44338	YES	YES
43	a	290.55	0.70875	YES	YES
44	a	291.83	10.75046	YES	YES
45	a	301.76	8.36295	YES	YES
46	a	305.20	0.23413	YES	YES
47	a	330.79	4.27035	YES	YES
48	a	335.84	3.73212	YES	YES
49	a	369.67	24.98536	YES	YES
50	a	379.08	17.60743	YES	YES

7.3. CP*-Protonation Pathway

TS_{23c}

BP86/SV(P) energy (au): -1622.0268068760

PBE0/def2-TZVPP energy (au): -1621.780505509
Cosmo dcm Total energy + OC corr.: -1621.8322443114

Zero point energy (au): 0.4998200
Entropy (kJ mol^{-1} K^{-1}): 0.93870
Chemical potential (kJ mol^{-1}): 1139.96

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-531.89	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.00000	- -
8	a	23.23	0.02549	YES YES
9	a	32.12	0.36365	YES YES
10	a	38.49	0.09288	YES YES
11	a	42.30	0.24134	YES YES
12	a	52.78	0.00588	YES YES
13	a	54.89	1.65395	YES YES
14	a	65.76	4.32408	YES YES
15	a	71.77	3.19229	YES YES
16	a	80.82	2.04763	YES YES
17	a	83.50	0.97270	YES YES
18	a	88.05	0.84486	YES YES
19	a	102.24	2.02284	YES YES
20	a	113.27	1.66736	YES YES
21	a	114.88	1.76108	YES YES
22	a	122.51	0.50117	YES YES
23	a	125.66	0.41266	YES YES
24	a	128.12	1.09287	YES YES
25	a	131.10	0.99280	YES YES
26	a	141.76	0.40792	YES YES
27	a	147.01	2.35113	YES YES
28	a	148.72	1.99256	YES YES
29	a	157.07	3.83036	YES YES
30	a	159.92	1.05861	YES YES
31	a	167.94	2.04691	YES YES

32	a	170.03	2.56755	YES	YES
33	a	178.48	0.97320	YES	YES
34	a	186.43	4.93613	YES	YES
35	a	189.87	1.85192	YES	YES
36	a	200.15	1.42748	YES	YES
37	a	206.79	2.15026	YES	YES
38	a	209.24	1.79473	YES	YES
39	a	223.21	2.13826	YES	YES
40	a	224.62	0.62804	YES	YES
41	a	236.52	0.64351	YES	YES
42	a	251.09	2.63118	YES	YES
43	a	259.68	4.72828	YES	YES
44	a	276.73	5.41121	YES	YES
45	a	282.36	8.08905	YES	YES
46	a	283.87	7.59772	YES	YES
47	a	287.37	3.82626	YES	YES
48	a	306.07	7.29233	YES	YES
49	a	310.89	4.93947	YES	YES
50	a	340.12	8.81495	YES	YES

3_c

BP86/SV(P) energy (au): -1622.0794498990

PBE0/def2-TZVPP energy (au):
Cosmo dcm Total energy + OC corr.:

Zero point energy (au): 0.5080744
Entropy (kJ mol^{-1} K^{-1}): 0.98090
Chemical potential (kJ mol^{-1}): 1142.84

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	3.34	0.01234	YES YES
8	a	30.51	0.12534	YES YES
9	a	34.64	0.50245	YES YES
10	a	41.15	0.85612	YES YES
11	a	46.60	0.14987	YES YES
12	a	51.22	0.03041	YES YES
13	a	58.25	2.35671	YES YES
14	a	64.59	1.40540	YES YES
15	a	69.61	3.09687	YES YES
16	a	70.31	1.33694	YES YES
17	a	76.61	0.14747	YES YES
18	a	81.76	0.46110	YES YES
19	a	91.92	0.51187	YES YES
20	a	95.86	1.78795	YES YES
21	a	101.14	1.02503	YES YES
22	a	104.80	0.60469	YES YES
23	a	114.96	0.89274	YES YES
24	a	116.68	0.85626	YES YES
25	a	118.53	2.06704	YES YES
26	a	135.45	1.16665	YES YES
27	a	143.27	0.35919	YES YES
28	a	146.92	0.17856	YES YES
29	a	155.70	0.95618	YES YES
30	a	160.12	2.44762	YES YES
31	a	162.70	2.14057	YES YES
32	a	169.44	10.20506	YES YES
33	a	180.96	1.79403	YES YES

34	a	194.75	5.11546	YES	YES
35	a	198.47	0.41220	YES	YES
36	a	206.05	2.52288	YES	YES
37	a	216.26	0.57810	YES	YES
38	a	220.82	0.16204	YES	YES
39	a	228.14	1.65386	YES	YES
40	a	234.91	0.08052	YES	YES
41	a	245.46	1.91130	YES	YES
42	a	253.25	16.90750	YES	YES
43	a	276.04	0.42368	YES	YES
44	a	283.04	25.25002	YES	YES
45	a	287.91	0.39752	YES	YES
46	a	292.43	9.08611	YES	YES
47	a	293.78	2.50009	YES	YES
48	a	295.93	2.65280	YES	YES
49	a	345.00	0.15993	YES	YES
50	a	350.36	0.96810	YES	YES

7.4. Oxidative Addition Pathway

TS_{26}

BP86/SV(P) energy (au): -1622.0644789630

PBE0/def2-TZVPP energy (au): -1621.836158933
Cosmo dcm Total energy + OC corr.: -1621.8880205634

Zero point energy (au): 0.5044694
Entropy (kJ mol^{-1} K^{-1}): 0.95668
Chemical potential (kJ mol^{-1}): 1138.73

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-341.79	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.00000	- -
8	a	15.88	0.06910	YES YES
9	a	30.60	0.23513	YES YES
10	a	34.75	0.69844	YES YES
11	a	38.73	0.09520	YES YES
12	a	43.20	0.22950	YES YES
13	a	48.75	0.15979	YES YES
14	a	57.02	0.68700	YES YES
15	a	57.88	0.67716	YES YES
16	a	67.46	1.41163	YES YES
17	a	70.45	6.15076	YES YES
18	a	81.43	0.32297	YES YES
19	a	88.33	1.45710	YES YES
20	a	94.45	1.30159	YES YES
21	a	101.35	0.67804	YES YES
22	a	104.62	0.30401	YES YES
23	a	120.37	1.12019	YES YES
24	a	131.33	0.77263	YES YES
25	a	137.04	0.49688	YES YES
26	a	143.22	0.41879	YES YES
27	a	148.14	0.64114	YES YES
28	a	154.55	1.73682	YES YES
29	a	156.89	0.79476	YES YES
30	a	158.92	2.27598	YES YES
31	a	167.92	1.67752	YES YES

32	a	179.36	0.57576	YES	YES
33	a	180.95	2.52708	YES	YES
34	a	184.65	6.09685	YES	YES
35	a	195.40	2.30261	YES	YES
36	a	197.85	3.82466	YES	YES
37	a	209.55	0.64464	YES	YES
38	a	214.10	1.22204	YES	YES
39	a	225.61	2.96910	YES	YES
40	a	230.92	10.90851	YES	YES
41	a	248.63	4.49528	YES	YES
42	a	257.63	6.18250	YES	YES
43	a	274.90	0.22027	YES	YES
44	a	277.99	1.04401	YES	YES
45	a	284.27	10.83323	YES	YES
46	a	291.64	5.83184	YES	YES
47	a	297.11	8.92083	YES	YES
48	a	304.10	4.85783	YES	YES
49	a	338.02	1.02342	YES	YES
50	a	350.03	2.89382	YES	YES

6

BP86/SV(P) energy (au): -1622.0649795350

PBE0/def2-TZVPP energy (au): -1621.834694474
Cosmo dcm Total energy + OC corr.: -1621.8868614781

Zero point energy (au): 0.5055858
Entropy (kJ mol^{-1} K^{-1}): 0.95984
Chemical potential (kJ mol^{-1}): 1142.20

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	24.67	0.08916	YES YES
8	a	32.83	0.20680	YES YES
9	a	33.74	0.19541	YES YES
10	a	38.73	0.43931	YES YES
11	a	42.84	0.10761	YES YES
12	a	49.89	0.25171	YES YES
13	a	54.41	1.62326	YES YES
14	a	60.45	1.34970	YES YES
15	a	62.50	0.14056	YES YES
16	a	68.51	4.92870	YES YES
17	a	81.17	2.11965	YES YES
18	a	81.95	0.35880	YES YES
19	a	87.62	1.25070	YES YES
20	a	96.77	1.41821	YES YES
21	a	101.21	0.52341	YES YES
22	a	117.66	1.90682	YES YES
23	a	124.64	0.72311	YES YES
24	a	135.09	2.69037	YES YES
25	a	145.11	1.44696	YES YES
26	a	146.38	0.83093	YES YES
27	a	154.40	1.04846	YES YES
28	a	158.05	0.32577	YES YES
29	a	160.61	1.76907	YES YES
30	a	167.06	3.43172	YES YES
31	a	176.60	1.51672	YES YES
32	a	181.20	1.30824	YES YES
33	a	183.66	6.14500	YES YES

34	a	195.43	4.44492	YES	YES
35	a	201.15	3.47602	YES	YES
36	a	205.93	0.46114	YES	YES
37	a	213.58	0.88817	YES	YES
38	a	217.77	4.23801	YES	YES
39	a	225.42	0.40747	YES	YES
40	a	243.50	6.52396	YES	YES
41	a	253.27	5.37579	YES	YES
42	a	274.29	0.13811	YES	YES
43	a	278.45	1.04708	YES	YES
44	a	284.93	11.23644	YES	YES
45	a	287.86	0.35261	YES	YES
46	a	294.70	11.80493	YES	YES
47	a	301.92	5.30199	YES	YES
48	a	331.30	7.22586	YES	YES
49	a	337.01	0.87516	YES	YES
50	a	347.49	0.87913	YES	YES

7.5. 1,2-Hydride Shift Pathway

TS_{24}

BP86/SV(P) energy (au): -1622.0723102940

PBE0/def2-TZVPP energy (au): -1621.849067506
Cosmo dcm Total energy + OC corr.: -1621.9030602032

Zero point energy (au): 0.5035400
Entropy (kJ mol^{-1} K^{-1}): 0.95959
Chemical potential (kJ mol^{-1}): 1136.19

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1	a	-681.92	0.00000	YES YES
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7		0.00	0.00000	- -
8	a	9.21	0.17306	YES YES
9	a	24.80	0.04299	YES YES
10	a	30.68	0.27726	YES YES
11	a	34.34	0.40717	YES YES
12	a	43.92	0.65209	YES YES
13	a	52.60	0.90631	YES YES
14	a	60.43	4.68327	YES YES
15	a	67.62	1.34438	YES YES
16	a	71.15	5.88117	YES YES
17	a	85.81	0.89234	YES YES
18	a	92.46	0.51855	YES YES
19	a	94.97	0.07167	YES YES
20	a	102.30	0.74202	YES YES
21	a	107.85	0.29672	YES YES
22	a	112.28	0.75756	YES YES
23	a	126.05	0.57975	YES YES
24	a	133.92	0.74410	YES YES
25	a	143.23	1.17812	YES YES
26	a	148.91	2.98285	YES YES
27	a	150.52	0.92211	YES YES
28	a	155.30	0.64894	YES YES
29	a	156.79	1.26741	YES YES
30	a	160.92	2.17615	YES YES
31	a	167.01	4.71137	YES YES

32	a	172.70	2.23727	YES	YES
33	a	181.40	0.58515	YES	YES
34	a	189.27	1.65145	YES	YES
35	a	193.40	0.95095	YES	YES
36	a	203.95	2.49839	YES	YES
37	a	209.61	0.98793	YES	YES
38	a	212.87	0.49871	YES	YES
39	a	232.50	5.35859	YES	YES
40	a	234.29	7.62961	YES	YES
41	a	246.11	0.35492	YES	YES
42	a	256.81	23.86859	YES	YES
43	a	263.46	5.26600	YES	YES
44	a	279.38	5.25281	YES	YES
45	a	280.58	0.71004	YES	YES
46	a	283.43	1.28109	YES	YES
47	a	297.30	3.17736	YES	YES
48	a	300.32	0.99434	YES	YES
49	a	307.48	24.64083	YES	YES
50	a	324.18	6.81167	YES	YES

7.6. Alternative Alkynes:

5_{b}_*E* (Ph):

BP86/SV(P) energy (au): -1813.7562076530

PBE0/def2-TZVPP energy (au): -1813.494739909
Cosmo dcm Total energy + OC corr.: -1813.5452880000

Zero point energy (au): 0.5629120
Entropy (kJ mol^{-1} K^{-1}): 1.00776
Chemical potential (kJ mol^{-1}): 1283.44

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	12.28	0.03685	YES YES
8	a	14.44	0.03738	YES YES
9	a	26.45	1.05772	YES YES
10	a	35.30	0.15660	YES YES
11	a	40.40	0.23791	YES YES
12	a	50.88	1.12525	YES YES
13	a	55.41	0.72863	YES YES
14	a	63.81	0.77476	YES YES
15	a	73.13	0.08944	YES YES
16	a	73.43	1.02012	YES YES
17	a	82.87	0.28089	YES YES
18	a	87.35	1.07378	YES YES
19	a	90.11	0.08502	YES YES
20	a	92.30	0.74302	YES YES
21	a	103.00	1.50666	YES YES
22	a	116.04	1.58695	YES YES
23	a	118.60	0.22548	YES YES
24	a	126.86	2.64503	YES YES
25	a	131.58	1.89910	YES YES
26	a	134.20	0.44679	YES YES
27	a	135.75	0.45896	YES YES
28	a	142.14	1.75674	YES YES
29	a	143.61	0.63525	YES YES
30	a	151.94	0.54883	YES YES
31	a	157.16	2.05659	YES YES

32	a	161.34	0.54342	YES	YES
33	a	168.30	0.72878	YES	YES
34	a	173.78	0.57626	YES	YES
35	a	179.32	1.06818	YES	YES
36	a	195.28	3.88878	YES	YES
37	a	198.15	1.83796	YES	YES
38	a	200.01	2.48165	YES	YES
39	a	223.53	1.06870	YES	YES
40	a	232.51	0.54693	YES	YES
41	a	244.67	4.12336	YES	YES
42	a	251.42	4.13094	YES	YES
43	a	277.25	0.07669	YES	YES
44	a	285.43	1.48609	YES	YES
45	a	292.12	0.70543	YES	YES
46	a	294.29	2.92532	YES	YES
47	a	302.92	5.38622	YES	YES
48	a	310.61	14.35956	YES	YES
49	a	315.92	4.76037	YES	YES
50	a	344.75	3.25431	YES	YES

5_a_*E* (Ph):

BP86/SV(P) energy (au): -1813.7579496390

PBE0/def2-TZVPP energy (au): -1813.495817152
Cosmo dcm Total energy + OC corr.: -1813.5462639756

Zero point energy (au): 0.5630714
Entropy (kJ mol^{-1} K^{-1}): 1.00521
Chemical potential (kJ mol^{-1}): 1284.40

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	10.75	0.05460	YES YES
8	a	14.66	0.06063	YES YES
9	a	24.65	0.19169	YES YES
10	a	37.43	0.84121	YES YES
11	a	45.75	0.10077	YES YES
12	a	52.72	1.00399	YES YES
13	a	56.15	0.46012	YES YES
14	a	61.38	0.61493	YES YES
15	a	66.36	1.50025	YES YES
16	a	66.92	0.34484	YES YES
17	a	80.71	0.16819	YES YES
18	a	82.28	1.31854	YES YES
19	a	97.19	1.27323	YES YES
20	a	104.41	0.36518	YES YES
21	a	110.96	1.73142	YES YES
22	a	115.44	1.84114	YES YES
23	a	121.05	0.34800	YES YES
24	a	131.34	0.42897	YES YES
25	a	139.78	2.49866	YES YES
26	a	142.07	1.18441	YES YES
27	a	144.97	0.57313	YES YES
28	a	149.07	0.21700	YES YES
29	a	154.24	0.67541	YES YES
30	a	155.75	2.00910	YES YES
31	a	161.66	2.71742	YES YES
32	a	169.45	1.97518	YES YES
33	a	174.30	0.19399	YES YES

34	a	176.38	0.41921	YES	YES
35	a	184.37	1.13743	YES	YES
36	a	193.05	2.88078	YES	YES
37	a	198.84	0.56595	YES	YES
38	a	202.15	2.35526	YES	YES
39	a	209.40	1.44037	YES	YES
40	a	223.40	0.02797	YES	YES
41	a	249.72	2.38573	YES	YES
42	a	252.15	2.95605	YES	YES
43	a	256.59	5.85324	YES	YES
44	a	282.79	0.04960	YES	YES
45	a	285.38	0.43239	YES	YES
46	a	291.04	15.30365	YES	YES
47	a	294.10	0.66430	YES	YES
48	a	300.44	2.20727	YES	YES
49	a	306.99	1.44403	YES	YES
50	a	343.15	3.81064	YES	YES

5_b_*E* (*p*-^{t}Bu):

BP86/SV(P) energy (au): -1970.8801592940

PBE0/def2-TZVPP energy (au): -1970.609424992
Cosmo dcm Total energy + OC corr.: -1970.6586695775

Zero point energy (au): 0.6715722
Entropy (kJ mol^{-1} K^{-1}): 1.11480
Chemical potential (kJ mol^{-1}): 1551.74

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	12.49	0.04406	YES YES
8	a	15.97	0.02717	YES YES
9	a	21.94	0.14674	YES YES
10	a	24.41	0.75481	YES YES
11	a	28.20	0.28905	YES YES
12	a	40.51	0.06498	YES YES
13	a	50.78	0.93527	YES YES
14	a	53.78	0.67853	YES YES
15	a	62.32	0.74531	YES YES
16	a	65.85	0.88645	YES YES
17	a	74.81	0.79866	YES YES
18	a	76.46	0.26896	YES YES
19	a	79.89	0.53601	YES YES
20	a	88.86	0.51373	YES YES
21	a	90.54	1.35776	YES YES
22	a	99.08	0.31155	YES YES
23	a	105.78	1.89100	YES YES
24	a	113.20	3.79373	YES YES
25	a	116.39	0.12972	YES YES
26	a	126.57	1.12906	YES YES
27	a	129.02	0.79979	YES YES
28	a	132.45	0.18514	YES YES
29	a	134.50	0.74871	YES YES
30	a	136.58	0.37702	YES YES
31	a	143.18	1.27474	YES YES
32	a	153.35	0.28054	YES YES
33	a	153.88	1.85623	YES YES

34	a	156.99	0.69661	YES	YES
35	a	168.81	0.99984	YES	YES
36	a	174.78	0.15293	YES	YES
37	a	177.60	0.91538	YES	YES
38	a	187.38	1.54314	YES	YES
39	a	195.90	3.84140	YES	YES
40	a	199.70	2.54102	YES	YES
41	a	202.55	0.35190	YES	YES
42	a	223.09	0.36967	YES	YES
43	a	233.68	2.50162	YES	YES
44	a	237.96	2.14673	YES	YES
45	a	249.86	0.90334	YES	YES
46	a	252.39	4.53340	YES	YES
47	a	271.52	1.14810	YES	YES
48	a	277.79	0.06748	YES	YES
49	a	285.15	1.61458	YES	YES
50	a	288.63	1.17889	YES	YES

5_a_*E* (*p*-^{t}Bu):

BP86/SV(P) energy (au): -1970.8821306890

PBE0/def2-TZVPP energy (au): -1970.611079156
Cosmo dcm Total energy + OC corr.: -1970.6606121385

Zero point energy (au): 0.6716705
Entropy (kJ mol^{-1} K^{-1}): 1.11156
Chemical potential (kJ mol^{-1}): 1552.73

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	11.64	0.02003	YES YES
8	a	13.89	0.07377	YES YES
9	a	17.76	0.06568	YES YES
10	a	30.14	0.84998	YES YES
11	a	34.73	0.10010	YES YES
12	a	46.82	0.28466	YES YES
13	a	51.20	0.22616	YES YES
14	a	53.33	0.18634	YES YES
15	a	56.69	0.65557	YES YES
16	a	63.22	0.39533	YES YES
17	a	66.58	2.27724	YES YES
18	a	67.04	0.26430	YES YES
19	a	82.24	1.17461	YES YES
20	a	93.78	0.87624	YES YES
21	a	102.94	0.81140	YES YES
22	a	109.23	1.60771	YES YES
23	a	114.66	0.43259	YES YES
24	a	120.98	2.33112	YES YES
25	a	126.43	0.66069	YES YES
26	a	131.58	1.16978	YES YES
27	a	136.43	1.80179	YES YES
28	a	139.56	2.65870	YES YES
29	a	144.33	0.10150	YES YES
30	a	145.35	0.71868	YES YES
31	a	149.77	0.59281	YES YES
32	a	153.38	1.40915	YES YES
33	a	155.20	0.20541	YES YES

34	a	161.92	1.82272	YES	YES
35	a	172.57	1.59432	YES	YES
36	a	175.52	0.13141	YES	YES
37	a	177.71	0.39839	YES	YES
38	a	184.73	0.07629	YES	YES
39	a	192.94	2.68054	YES	YES
40	a	197.17	3.13414	YES	YES
41	a	203.96	0.46114	YES	YES
42	a	218.72	1.35497	YES	YES
43	a	220.83	3.59458	YES	YES
44	a	223.91	0.43463	YES	YES
45	a	251.04	3.83809	YES	YES
46	a	258.08	0.16608	YES	YES
47	a	261.64	1.78960	YES	YES
48	a	272.30	0.24233	YES	YES
49	a	281.77	0.10349	YES	YES
50	a	288.01	0.23002	YES	YES

5_b_*E* (Cy):

BP86/SV(P) energy (au): -1817.3540754210

PBE0/def2-TZVPP energy (au): -1817.109679092
Cosmo dcm Total energy + OC corr.: -1817.1571208149

Zero point energy (au): 0.6301801
Entropy (kJ mol^{-1} K^{-1}): 1.04654
Chemical potential (kJ mol^{-1}): 1453.35

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	13.33	0.03589	YES YES
8	a	15.56	0.01936	YES YES
9	a	28.62	0.89790	YES YES
10	a	32.92	0.04086	YES YES
11	a	42.04	0.07808	YES YES
12	a	44.35	0.12123	YES YES
13	a	51.54	0.73087	YES YES
14	a	53.85	1.60137	YES YES
15	a	67.30	0.43597	YES YES
16	a	70.47	1.11878	YES YES
17	a	73.21	0.18789	YES YES
18	a	77.62	0.19111	YES YES
19	a	85.97	0.40644	YES YES
20	a	90.30	0.13625	YES YES
21	a	93.74	1.35649	YES YES
22	a	100.77	0.21736	YES YES
23	a	106.06	2.65010	YES YES
24	a	111.63	2.16806	YES YES
25	a	118.24	0.25518	YES YES
26	a	126.52	1.38336	YES YES
27	a	130.59	0.62755	YES YES
28	a	134.27	0.61973	YES YES
29	a	136.52	0.51524	YES YES
30	a	141.04	1.04198	YES YES
31	a	144.41	0.71278	YES YES
32	a	147.80	0.44673	YES YES
33	a	153.49	1.04115	YES YES

34	a	158.02	0.41729	YES	YES
35	a	163.80	1.03725	YES	YES
36	a	173.28	0.72036	YES	YES
37	a	175.24	0.62907	YES	YES
38	a	191.79	2.07683	YES	YES
39	a	196.83	4.28352	YES	YES
40	a	200.38	1.44594	YES	YES
41	a	221.49	0.05852	YES	YES
42	a	235.45	5.86885	YES	YES
43	a	250.66	3.86433	YES	YES
44	a	258.82	0.35877	YES	YES
45	a	278.63	0.01176	YES	YES
46	a	284.95	0.61796	YES	YES
47	a	291.14	0.26924	YES	YES
48	a	299.09	5.92499	YES	YES
49	a	302.96	15.11602	YES	YES
50	a	306.31	5.62720	YES	YES

5_a_*E* (Cy):

BP86/SV(P) energy (au): -1817.3502419790

PBE0/def2-TZVPP energy (au): -1817.105347121
Cosmo dcm Total energy + OC corr.: -1817.1526943984

Zero point energy (au): 0.6301602
Entropy (kJ mol^{-1} K^{-1}): 1.03983
Chemical potential (kJ mol^{-1}): 1454.64

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	11.84	0.03341	YES YES
8	a	13.80	0.09640	YES YES
9	a	22.47	0.12548	YES YES
10	a	35.93	0.19807	YES YES
11	a	37.68	0.53334	YES YES
12	a	48.81	0.63366	YES YES
13	a	51.08	0.04531	YES YES
14	a	56.47	0.39985	YES YES
15	a	65.19	0.12463	YES YES
16	a	69.10	2.93004	YES YES
17	a	70.27	0.49067	YES YES
18	a	85.90	0.60610	YES YES
19	a	91.30	0.58059	YES YES
20	a	96.64	2.12955	YES YES
21	a	105.03	0.22172	YES YES
22	a	111.67	0.94086	YES YES
23	a	114.28	0.31968	YES YES
24	a	115.51	1.81266	YES YES
25	a	129.52	0.19795	YES YES
26	a	138.49	2.56742	YES YES
27	a	140.24	0.80090	YES YES
28	a	142.97	1.18339	YES YES
29	a	146.47	0.80563	YES YES
30	a	147.78	0.30862	YES YES
31	a	152.21	0.56132	YES YES
32	a	157.83	2.79394	YES YES
33	a	165.35	1.73517	YES YES

34	a	171.51	0.21425	YES	YES
35	a	173.20	1.67893	YES	YES
36	a	175.22	0.30644	YES	YES
37	a	186.39	0.16553	YES	YES
38	a	195.44	3.58941	YES	YES
39	a	198.99	1.71236	YES	YES
40	a	203.96	0.84859	YES	YES
41	a	221.13	2.18279	YES	YES
42	a	222.86	1.81531	YES	YES
43	a	249.60	4.23580	YES	YES
44	a	255.80	0.25777	YES	YES
45	a	282.96	0.06526	YES	YES
46	a	284.14	0.45945	YES	YES
47	a	289.41	16.60780	YES	YES
48	a	292.54	0.34032	YES	YES
49	a	299.75	1.60524	YES	YES
50	a	306.31	0.62018	YES	YES

5_b_*E* (^{t}Bu):

BP86/SV(P) energy (au): -1739.9769356010

PBE0/def2-TZVPP energy (au): -1739.742644013
Cosmo dcm Total energy + OC corr.: -1739.7904852748

Zero point energy (au): 0.5926781
Entropy (kJ mol^{-1} K^{-1}): 1.01390
Chemical potential (kJ mol^{-1}): 1362.25

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	8.81	0.07790	YES YES
8	a	19.58	0.06092	YES YES
9	a	28.74	0.78516	YES YES
10	a	40.00	0.09063	YES YES
11	a	52.35	1.91984	YES YES
12	a	55.40	0.05651	YES YES
13	a	65.20	1.44349	YES YES
14	a	68.80	0.75102	YES YES
15	a	72.34	0.82855	YES YES
16	a	76.91	0.14085	YES YES
17	a	81.89	0.68605	YES YES
18	a	89.76	0.13807	YES YES
19	a	90.90	1.15197	YES YES
20	a	94.15	0.31822	YES YES
21	a	110.56	4.13652	YES YES
22	a	112.85	0.10362	YES YES
23	a	121.74	1.02708	YES YES
24	a	129.39	1.04636	YES YES
25	a	132.28	0.59098	YES YES
26	a	135.38	1.26002	YES YES
27	a	139.10	0.06938	YES YES
28	a	139.63	0.47077	YES YES
29	a	148.72	0.17882	YES YES
30	a	152.73	1.10531	YES YES
31	a	156.99	0.11969	YES YES
32	a	163.12	0.72801	YES YES
33	a	168.16	1.65382	YES YES

34	a	177.60	0.18019	YES	YES
35	a	187.39	0.61866	YES	YES
36	a	196.23	5.08040	YES	YES
37	a	198.16	2.68920	YES	YES
38	a	202.49	0.34478	YES	YES
39	a	223.77	0.36711	YES	YES
40	a	224.75	1.53878	YES	YES
41	a	244.51	4.25639	YES	YES
42	a	253.52	2.68482	YES	YES
43	a	256.86	1.91821	YES	YES
44	a	277.87	0.43385	YES	YES
45	a	278.03	0.17821	YES	YES
46	a	285.17	0.46674	YES	YES
47	a	290.57	0.21317	YES	YES
48	a	293.58	0.22812	YES	YES
49	a	300.38	1.04051	YES	YES
50	a	308.58	22.42605	YES	YES

5_a_*E* (^{t}Bu):

BP86/SV(P) energy (au): -1739.9830821250

PBE0/def2-TZVPP energy (au): -1739.748718674
Cosmo dcm Total energy + OC corr.: -1739.7963996820

Zero point energy (au): 0.5922935
Entropy (kJ mol^{-1} K^{-1}): 1.00997
Chemical potential (kJ mol^{-1}): 1362.44

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	12.73	0.03364	YES YES
8	a	18.70	0.19323	YES YES
9	a	28.06	0.08862	YES YES
10	a	41.91	0.67869	YES YES
11	a	48.50	0.15364	YES YES
12	a	54.11	1.41625	YES YES
13	a	58.28	0.01133	YES YES
14	a	64.95	1.64991	YES YES
15	a	72.82	0.47708	YES YES
16	a	76.75	0.21267	YES YES
17	a	83.47	1.74372	YES YES
18	a	94.10	0.20291	YES YES
19	a	97.31	1.27255	YES YES
20	a	101.96	0.37548	YES YES
21	a	113.24	2.95585	YES YES
22	a	118.50	0.07922	YES YES
23	a	122.16	1.25984	YES YES
24	a	131.06	0.28839	YES YES
25	a	140.59	2.69605	YES YES
26	a	142.83	0.79284	YES YES
27	a	147.47	0.34307	YES YES
28	a	149.25	0.43845	YES YES
29	a	152.67	0.19575	YES YES
30	a	157.57	2.01287	YES YES
31	a	166.61	2.96356	YES YES
32	a	170.15	1.58692	YES YES
33	a	174.09	0.41478	YES YES

34	a	176.36	0.49712	YES	YES
35	a	183.12	0.18707	YES	YES
36	a	193.81	4.98725	YES	YES
37	a	198.61	0.94885	YES	YES
38	a	203.70	1.25993	YES	YES
39	a	211.24	0.54461	YES	YES
40	a	219.06	0.37044	YES	YES
41	a	223.41	0.03298	YES	YES
42	a	249.46	3.63320	YES	YES
43	a	252.12	3.99298	YES	YES
44	a	277.82	5.10803	YES	YES
45	a	282.04	0.06133	YES	YES
46	a	284.32	0.37695	YES	YES
47	a	290.72	0.06653	YES	YES
48	a	291.35	14.71397	YES	YES
49	a	292.86	0.42501	YES	YES
50	a	300.47	1.39317	YES	YES

5_a_*Z*:

BP86/SV(P) energy (au): -1622.1380723270

PBE0/def2-TZVPP energy (au): -1621.910189416
Cosmo dcm Total energy + OC corr.: -1621.9586387654

Zero point energy (au): 0.5104195
Entropy (kJ mol^{-1} K^{-1}): 0.93161
Chemical potential (kJ mol^{-1}): 1160.13

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	10.17	0.04648	YES YES
8	a	29.61	0.30976	YES YES
9	a	41.21	0.16442	YES YES
10	a	44.67	0.05522	YES YES
11	a	54.53	0.21623	YES YES
12	a	59.89	1.46407	YES YES
13	a	68.74	0.01998	YES YES
14	a	77.76	4.01501	YES YES
15	a	89.32	2.36232	YES YES
16	a	96.80	0.14047	YES YES
17	a	100.92	1.25185	YES YES
18	a	105.37	0.11143	YES YES
19	a	110.71	1.39418	YES YES
20	a	112.76	0.69273	YES YES
21	a	114.55	0.09646	YES YES
22	a	123.58	1.07841	YES YES
23	a	130.64	0.18323	YES YES
24	a	134.23	0.30192	YES YES
25	a	140.08	1.56199	YES YES
26	a	145.07	1.19501	YES YES
27	a	148.66	0.27006	YES YES
28	a	151.45	0.93064	YES YES
29	a	159.98	1.72785	YES YES
30	a	162.30	0.07915	YES YES
31	a	169.31	2.17582	YES YES
32	a	182.31	0.87691	YES YES

33	a	184.22	2.29597	YES	YES
34	a	193.62	4.04839	YES	YES
35	a	199.26	1.10142	YES	YES
36	a	208.92	0.90792	YES	YES
37	a	213.76	1.44557	YES	YES
38	a	224.69	0.04364	YES	YES
39	a	233.43	1.41989	YES	YES
40	a	250.64	4.00891	YES	YES
41	a	276.54	0.06210	YES	YES
42	a	280.63	0.00856	YES	YES
43	a	288.62	1.41947	YES	YES
44	a	295.34	12.37929	YES	YES
45	a	301.35	5.08713	YES	YES
46	a	307.00	4.64815	YES	YES
47	a	323.12	13.10307	YES	YES
48	a	354.62	1.37006	YES	YES
49	a	367.29	8.19076	YES	YES
50	a	381.15	10.18261	YES	YES

5_b_*Z*:

BP86/SV(P) energy (au): -1622.1488115210

PBE0/def2-TZVPP energy (au): -1621.921753263
Cosmo dcm Total energy + OC corr.: -1621.9703104288

Zero point energy (au): 0.5106428
Entropy (kJ mol^{-1} K^{-1}): 0.94226
Chemical potential (kJ mol^{-1}): 1158.13

Vibrational Spectrum (first 50 lines):

# mode	symmetry	wave number	IR intensity	selection rules
#		cm**(-1)	km/mol	IR RAMAN
1		0.00	0.00000	- -
2		0.00	0.00000	- -
3		0.00	0.00000	- -
4		0.00	0.00000	- -
5		0.00	0.00000	- -
6		0.00	0.00000	- -
7	a	16.11	0.11114	YES YES
8	a	21.73	0.50063	YES YES
9	a	31.61	0.25009	YES YES
10	a	49.01	1.09454	YES YES
11	a	53.78	0.58170	YES YES
12	a	60.85	0.33364	YES YES
13	a	62.44	0.34908	YES YES
14	a	74.73	1.55047	YES YES
15	a	79.30	1.13983	YES YES
16	a	81.76	0.71733	YES YES
17	a	85.75	2.43562	YES YES
18	a	95.49	2.15319	YES YES
19	a	99.08	0.59658	YES YES
20	a	114.09	0.18551	YES YES
21	a	117.13	0.18398	YES YES
22	a	121.13	1.10655	YES YES
23	a	123.80	0.74875	YES YES
24	a	130.60	0.31012	YES YES
25	a	133.55	0.06107	YES YES
26	a	138.60	0.77949	YES YES
27	a	142.53	0.25828	YES YES
28	a	144.29	0.66827	YES YES
29	a	147.62	0.86184	YES YES
30	a	162.58	1.63555	YES YES
31	a	169.76	1.63338	YES YES
32	a	177.58	0.96690	YES YES
33	a	186.63	1.37761	YES YES

34	a	189.64	1.17040	YES	YES
35	a	199.65	3.41899	YES	YES
36	a	205.33	1.41818	YES	YES
37	a	217.16	0.00630	YES	YES
38	a	222.64	0.88687	YES	YES
39	a	228.80	7.88525	YES	YES
40	a	247.41	3.53765	YES	YES
41	a	275.57	0.25637	YES	YES
42	a	282.26	0.44338	YES	YES
43	a	290.55	0.70875	YES	YES
44	a	291.83	10.75046	YES	YES
45	a	301.76	8.36295	YES	YES
46	a	305.20	0.23413	YES	YES
47	a	330.79	4.27035	YES	YES
48	a	335.84	3.73212	YES	YES
49	a	369.67	24.98536	YES	YES
50	a	379.08	17.60743	YES	YES

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